California Environmental Protection Agency



### Air Resources Board

# PLANNED AIR POLLUTION RESEARCH

**Fiscal Year 2006-2007** 

July 2006

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#### Summary

This report presents the Air Resources Board's planned air pollution research for the fiscal year 2006-2007. Thirty-four projects are proposed. Twenty-one projects are recommended for funding and seven are recommended if funding is available. This research portfolio is organized into four main areas of research: Health and Welfare Effects, Exposure Assessment, Technology Advancement and Pollution Prevention, and Global Air Pollution. This year the Board is expecting to receive funds specific for climate change research from the Legislature. In response to the Governor's climate change targets, the Board requested funds to focus on various areas of research in order to achieve those targets. The research included in this year's plan is in direct response and in accordance with achieving the Governor's climate change reduction goals.

Another very important area is environmental justice (EJ). Over the last few fiscal years, the Board has invested over a \$1 million dollars into areas of environmental justice, such as developing community tools for exposure assessment, and investigating health effects. Although this year's plan does not have a dedicated set of projects to address environmental justice, EJ aspects and factors can be found throughout several projects in other subject areas.

This annual plan proposes research in the four areas mentioned above, with a significant effort to characterize and assess the behavior of pollutants in the atmosphere, and develop and improve technologies to reduce and control emissions, especially greenhouse. The proposed budget for the recommended projects is approximately \$5,000,000.

#### Introduction

The Air Resources Board (ARB) sponsors a comprehensive program of research addressing the causes, effects, and possible solutions to air pollution problems in California, and provides support for establishing ambient air quality standards. The Board's research program was established by the Legislature in 1971 (Health and Safety Code Sections 39700 et seq.) to develop a better understanding of the various aspects of air pollution, including air pollution's effects on health and the environment, the atmospheric reactions and transport of pollutants, and the inventory and control of air polluting emissions. In recent years, several legislative mandates have expanded and further defined the scope of the program.

The ARB's mission to protect California's public health, welfare, and ecological resources is supported through a Strategic Plan for Research covering the years 2001-2010. The Strategic Plan is based on the ARB's regulatory priorities for the next several years and provides direction for the ARB's research program. The four main areas of research identified in the Strategic Plan are: Health and Welfare Effects, Exposure Assessment, Technology Advancement and Pollution Prevention, and Global Air Pollution. They are also the categories that guide this plan. These areas encompass the comprehensive mission of ARB's air pollution research. The Strategic Plan can be found at http://www.arb.ca.gov/research/apr/apr.htm.

The proposed research projects are not intended to be exhaustive or exclusive. Unanticipated opportunities, unique or innovative study approaches, or urgency may lead to consideration of other projects.

**Objective of the Research Program.** The goal of the research program is to provide the timely scientific and technical information that will allow the Board and local districts to make the public policy decisions necessary to implement an effective air pollution control program in California.

Process for Developing this Research Plan. The Board sends out a public solicitation inviting and encouraging the public to contribute ideas for project consideration. Members of the public, the academic community, and ARB staff submit research ideas. To aid in the evaluation, the Board's Executive Officer established committees, led by ARB staff, to review research ideas. In response to this years solicitation, approximately 200 research ideas were submitted. Proposed projects were examined for relevance to regulatory questions facing the Board and modified as necessary. Committee members then prioritized candidate projects in order of urgency and importance. The Board's scientific external review committee, the Research Screening Committee (RSC), which was established by the Health and Safety Code section 39705, reviewed these candidate projects. The list of projects, along with comments from the RSC, was forwarded to the Executive Research Review Committee, whose members are the Executive Officer, her three deputies, and the Chief of the Research Division. The Executive Research Review Committee reviewed all of the proposed projects and established project priorities. Selected projects are then placed into two categories: 1) those that are recommended for funding, and 2) those that are recommended if funding is available. The Research Screening Committee reviewed the selected projects and recommended the Plan to the Board.

*Implementation of the Plan.* The next step for projects approved in the plan will be their development into full research projects. The submission and selection of an idea does not guarantee a resulting contract for the submitter. Rather, the ARB is required to consider public California universities for expertise to execute these projects. If the universities do not possess the expertise, then a public solicitation is issued or a sole source contract is awarded. There is a list serve that can be subscribed to in order to receive updates on research activities. Visit <u>www.arb.ca.gov/listserv/research/research.htm</u> for more information.

**Research Budget.** The 21 recommended projects total approximately \$5,000,000. The allocations for the proposed recommended projects among research categories are as follows:

RESEARCH CATEGORY	BUDGET
Health and Welfare Effects	\$1,000,000
Exposure Assessment	\$1,967,000
Technology Advancement and Pollution Prevention	\$850,000
Global Air Pollution	\$1,050,000
TOTAL	\$4,867,000

**Project Co-sponsorships.** The Research Division is continually looking for cofunding opportunities and other ways to leverage the state's research dollars. This effort allows the ARB to be part of projects and studies that may otherwise be out of the state's fiscal reach. ARB has had great success in working with other research organizations and has been part of multimillion-dollar studies with nominal cash contributions. Several of the projects in this plan have either confirmed or have potential cofunding dollars included in the cost category.

*Summaries of Past Research.* Ongoing research projects and projects completed since the beginning of 1989 are summarized in the Research Division's publication, Air Pollution Research, at <u>www.arb.ca.gov/research/apr/past/past.htm</u>.

Electronic copies of all of the Research Division's final reports are available for downloading at the same web site.

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**HEALTH AND WELFARE EFFECTS** – the projects funded under this section are dedicated to the memory of Dr. William Friedman, former ARB Board Member who passed away on August 25, 2005. Dr. Friedman was a strong advocate for the ARB's health research and guided many of the projects that have increased the Board's understanding of how air pollution affects human health, especially children's health.

#### Human Health Effects – *Recommended Projects*

Source-Oriented Ambient Aerosol Biosampling and Toxicology, \$400,000......9 To examine the pulmonary and cardiovascular health effects of both laboratory and ambient particles.

To derive detailed assessments of the impact of particulate air pollution on allcause and cause specific mortality in California and investigate whether critical exposure windows exist in the relationship between air pollution and mortality in California.

To conduct multiple sensitivity analyses as part of the ongoing study which aims to provide a prospective examination of the disease and mortality experience of over 100,000 current and former female public school teachers and administrators.

#### Recommended if funding available

Data Validation and Support of Continuous Monitoring at the Fresno Supersite as part of FACES, \$300,000......15

To keep the Fresno Supersite in operation through December 2007 in order to assist ARB in researching the health and welfare effects of PM exposure and for evaluating long term particulate trends at the Fresno Supersite.

To study the effect of ambient particulate matter air pollution on the central nervous system.

To develop a mobile facility to conduct animal inhalation studies to various PM sources at a variety of different sites and during different seasons.

#### Atmospheric Processes – *Recommended Projects*

To develop the capability for routine application of inverse modeling techniques in combination with satellite measurements to improving the retrospective and predictive capabilities of models applied to ozone and PM and the movement of goods in California.

To develop a universal land use regression model for predicting NO<sub>2</sub> and PM2.5 concentrations for use in burden of illness and epidemiologic investigations across California.

Flux Measurements of Biogenic Precursors to Ozone and Particulate Matter in the Central Valley, \$400,000 ......25

To evaluate biogenic volatile organic compound (BVOC) emission model performance and improve the representation of emissions and atmospheric processes using in-situ measurements of BVOC emissions, micrometeorology and atmospheric chemical reactions within selected agricultural landscapes over growing seasons.

Deployment of a Novel Aerosol Mobility/Mass Spectrometer for Quantitative Chemical Analysis of Organic Aerosols from Mobile Sources, \$240,000 ............27

To deploy an aerosol mobility/mass spectrometer in collaboration with ongoing field measurements through the Southern California PM Center and target light and heavy duty freeways, the L.A. shipping port, and LAX airport.

To identify the contribution of fossil fuel combustion, wood burning, meat cooking, and natural direct input to the burden of size-resolved carbonaceous PM and volatile organic compounds.

#### **Emission Inventory – Recommended Projects**

Assessing Near-Field Exposures from Distributed Combustion Sources, \$250,000

Characterize the near-field components of intake fraction attributable to certain important distributed combustion sources. In doing so, improve the base of knowledge for assessing the near-field exposure impacts of sources that emit close to people. To support continued and expanded monitoring operations at Bodega Bay for the purpose of quantifying emissions of CO,  $NO_X$ , and  $SO_X$  from offshore shipping channels. Careful analysis of the dimensions and sum of these pollutant plumes will help characterize the regional pollutant sources from offshore shipping.

#### Recommended if funding available

To provide a more complete picture of the products formed from atmospheric reactions of monocyclic aromatic hydrocarbons and their yields and the formation routes to nitro-PACs in the atmosphere and the role of  $NO_2$  in their formation.

To monitor pollutants from light duty vehicles in three regions of California, the Los Angeles basin, the central valley and the Bay area.

Secondary Port Truck Activity Study, \$150,000......40

To characterize the fleet of trucks that make secondary trips related to the movement of international containerized goods in the South Coast, identify distribution center facilities that service these containerized goods, and quantify emissions associated with those truck trips, and activity of trucks and other equipment operating at distribution centers.

#### TECHNOLOGY ADVANCEMENT AND POLLUTION PREVENTION

#### Clean Air Technologies – Recommended Projects

To adapt and test a low-cost datalogging particle monitor using commercial smoke-alarm sensors developed by UC Berkeley for third-world use in California conditions.

To identify the most promising emission control technologies for ocean-going vessels considering all possible technologies, especially those not currently used on marine vessels.

To fill knowledge gaps to provide the necessary data to facilitate life cycle assessments needed for programs implementing greenhouse gas emissions reductions and the evaluations required under AB1007.

Engine Lubricating Oil Impacts on Mobile Source PM Emissions, \$100,000......49 To characterize the significance of lube oil in PM formation and to determine whether lube oil can be formulated to reduce in-use PM emissions from mobile sources, if it is demonstrated that lube oil is the largest contributor to PM from mobile sources.

#### Clean Air Technologies – Recommended if funding avaliable

Diesel Engine Crankcase Blow-By and Diesel High PM Emitters: Determination of Contributions to Ambient Particulate Matter and Potential Health Effects, \$350,000

To determine the influence of diesel engine blow-by and high PM emitter source profiles on chemical mass balance modeling results, while the second objective would be to investigate the toxicity of these emissions.

#### **GLOBAL AIR POLLUTION**

#### Climate Change– Recommended Projects

To develop an algorithm for quantifying the life cycle emission effects of any measure that ARB staff may propose to meet the California GHG emission-reduction goals.

To quantify the populations of commercial systems by the type of HFC used, the application, the emissions rate, and the turnover rate to develop a baseline inventory for California.

#### Climate Change- Recommended if funding available

Economic Impacts and Benefits of Climate Change Control Strategies, \$250,000

To improve ARB's in-house capability to model the economic impact of climate change control strategies.

To improve the ability of climate model to reproduce observed long-term trends in background tropospheric ozone, and to better understand the factors controlling the concentrations and trends of tropospheric OH, and the implications for the methane lifetime and for methane trends.

### TITLE: Source-Oriented Ambient Aerosol Biosampling and Toxicology

**PROBLEM:** Numerous epidemiological studies demonstrate a correlation between ambient particulate matter concentrations and increased morbidity and mortality, yet the mechanistic and causal links between health effects and particulate matter concentrations have eluded identification. One possible confounder is that ambient particles derive from a range of sources and experience a range of atmospheric processes that may alter their toxicity. Direct exposures of animals to emissions neglects atmospheric photochemistry that may enhance toxicity, while exposure to ambient or concentrated ambient particles (CAPs) combines the effect of many sources so does not elucidate which source contributes to the toxicity. The use of an ultrafine single particle mass spectrometer (RSMS-II) could be used to selectively collect ambient aerosol particles with a series of SKC biosamplers attached to a Versatile Aerosol Concentration System (VACES) and instill these samples to deduce their toxicity.

**PREVIOUS WORK:** Kent Pinkerton of the University of California, Davis (UCD) has extensive experience exposing rodents to CAPs to determine their relative toxicity and toxicity mechanisms. Anthony Wexler of UCD has developed an ultrafine single particle mass spectrometer that has been used in four of EPA's supersites (Atlanta, Houston, Pittsburgh and Baltimore) to determine the composition of individual ultrafine particles and associate these compositions with their sources. Studies to examine the health effects in animals have been done in Davis, Sacramento and Fresno. These studies have demonstrated unique responses to particle exposure with differences noted based on particle size and composition.

**OBJECTIVE:** The objective is to assess the toxicity of source-oriented ambient samples by using a single particle mass spectrometer, a VACES, and many biosamplers to collect ambient samples that are characteristic of a given source. Individuals are exposed to a wide range of atmospheric particle sizes and compositions. UCD has obtained an award from the United States Environmental Protection Agency for its San Joaquin Valley Aerosol Health Effects Research Center (SAHERC). Scientists from the center will examine the pulmonary and cardiovascular health effects of both laboratory and ambient particles. The ambient particles will be collected near Fresno using a VACES attached to a SKC biosampler. The toxicity of the particles will be assessed by instillation into rodents and subsequent toxicity studies. Typically, individuals at a given location are exposed to a range of particle compositions depending on the wind direction, which sources are in the vicinity, the mixing state of the atmosphere, and other factors. Collecting one VACES biosample mixes the particles from various sources together obscuring the relative toxicity of each.

**DESCRIPTION:** With RSMS-II, investigators are able to collect single particle spectra over the size range from about 40 nm to 1.2  $\mu$ m, and classify them in real time using ART2a (this was done at the Houston supersite). That is, each particle analyzed possesses a mass spectrum and, in real time, these spectra are classified into similar groups indicative of their primary emissions source and the degree of their atmospheric processing. By sampling over weeks, different meteorological conditions prevail bringing different primary emissions to the sampling site and causing different degrees of

secondary processing, which in turn cause the particles to have different compositions and different levels of toxicity.

**Methods (Sample Collection):** Investigators will locate the RSMS-II ultrafine single particle mass spectrometer and a VACES in biosampler mode side by side in Fresno where other SAHERC ambient samples are collected. RSMS-II will be modified in two ways. First, they will only sample at one size, 200 µm, characteristic of the ultrafine size range. Second, they will use the real-time categorization capabilities of RSMS-II to control the sampling of ambient particles in real time, as described in a moment. The VACES will be used in biosampler mode but it too will be modified such that 10 biosamplers will be employed. A 10-position rotary valve will direct the output from VACES to one of the biosamplers. RSMS-II will control the rotary valve such that two biosamplers collect fine and ultrafine particles characteristic of one source profile. A source profile will be defined by either (1) detection of a single particle type or (2) detection of multiple particle types that often appear together. Sites are often influenced by a range of primary particle sources and secondary processing, but 9 source categories should be sufficient. The 10<sup>th</sup> biosampler will collect samples when the source profile detected does not fit into one of the first nine.

**Methods (Toxicity):** Young adult Sprague Dawley rats will be used to test the relative toxicity of ambient particles collected via the VACES for each biosampler. A precise concentration of biosampler material will be instilled into the lungs of each individual animal. Following 24 hours post-instillation, the lungs will be lavaged to determine recovered cell numbers, cell viability, phagocytic index and the cell differential. Indicators of oxidative stress such as glutathione, heme oxygenase and selected cytokines will be measured in lung tissues. For each biosampler material, eight animals will be analyzed. Sham controls will receive an equivalent instillation of sterile saline. Of the 40 biosamples collected, toxicity will be tested on the 28 most prevalent samples.

#### Tasks:

- 1. Build and test RSMS-II/VACES/Biosampler using Davis ambient air (4 months)
- 2. Establish facility in Fresno (primarily SAHERC funded) (in parallel with #1)
- 3. Install and operate RSMS-II and collect biosamples for summer and winter seasons
- 4. Test biosamples for toxicity (in parallel with #3)
- 5. Identify sources of particles classes (in parallel with #3)
- 6. Associate toxicity with source class (4 months)
- 7. Publish results and write final report (4 months)

**BENEFITS:** Californians breathe air pollution particles emitted by a wide range of sources. For the first time, investigators will extract particulate samples from the atmosphere that are associated with the major sources of pollution in the San Joaquin Valley of California and deduce the toxicity of these samples by instillation in rodents. The result will be relative toxicity index for particles derived from each source category.

**COST:** \$400,000 (an additional \$361,496 will be contributed by EPRI)

### TITLE: Extending the American Cancer Society Study of Particulate Air Pollution and Mortality to the Intra-urban Scale in California

**PROBLEM:** Studies using the American Cancer Society (ACS) cohort to assess the relation between particulate air pollution and mortality rank among the most influential and widely cited. The original study, a reanalysis that introduced new random effects methods and spatial analytic techniques, and recent studies with longer follow-up and improved exposure data have all demonstrated statistically significant and substantively large air pollution effects on all cause and cause-specific mortality. Due to this robust association and a lack of other studies on the long-term effects, the ACS studies in addition to the Six-Cities study have proven important to government regulatory interventions and health burden assessments. The assessment of air pollution exposure using only community average concentrations likely underestimates the health burden attributable to elevated concentrations in the vicinity of sources. Health effects may be larger around sources, and these effects are diminished when using average concentrations for the entire community. At present, there are no specific estimates of mortality in relation to particulate air pollution for the entire state California.

**PREVIOUS WORK:** Recently the first assessment of mortality and particulate air pollution estimates was published for the intra-urban or within-city scale in Los Angeles. Results suggest the chronic health effects associated with intra-urban gradients in exposure to PM2.5 may be even larger than previously reported across metropolitan areas. Observed effects were nearly three times greater than in models relying on between-community exposure contrasts. Given these remarkable findings, a need exists to investigate whether the findings hold for other parts of California and are robust to alternative measures of exposure assessment and confounding control. Researchers have also been investigating whether there are temporal patterns in the relative risk of mortality from air pollution. These studies suggest that with increasing mobile source contributions are *increased* doseresponse functions over time.

**OBJECTIVE:** The objectives are to derive detailed assessments of the impact of particulate air pollution on all-cause and cause specific mortality in California and investigate whether critical exposure windows exist in the relationship between air pollution and mortality in California.

**DESCRIPTION:** Over 40,000 subjects have been identified in the ACS cohort who will serve as the study population. These subjects are widely distributed across California, giving good coverage of much of the population of the State. For the first time, subjects will be geocoded to their home address at time of enrolment. Previous studies have been restricted to zip code areas, limiting our ability to assign exposures based on proximity to source.

As a basis for exposure assessment, newly developed estimates will be utilized for the California Teachers Cohort Study. These estimates will be extended with advanced Bayesian Maximum Entropy kriging models to allow for spatiotemporal exposure assignment with explicit incorporation for errors in the exposure estimates. Following current national analysis, refined exposure data will be used to assess whether critical exposure windows exist in the mortality experience. Because the data will be geocoded

researchers will also have the opportunity to assess proximity to sources such as the Port of Los Angeles and the major highways in the state.

The standard suite of 44 individual confounders documented in earlier ACS studies will be employed investigating air pollution health effects. These variables control for lifestyle, dietary, demographic, occupational, and educational influences that may confound the air pollution-mortality association. Eight ecological variables will be assembled for the ZCAs to control for "contextual" neighbourhood confounding. "Contextual" effects occur when individual differences in health outcome associate with the grouped variables that represent the social, economic, and environmental settings where the individuals live, work or spend time (e.g., e.g., poverty or crime rate in a neighborhood).

**BENEFITS:** California currently has no state-wide estimates of mortality to support policymaking and regulatory activities. Extension of the ACS study to address scientific uncertainties and to derive estimates specific to California will provide information that will allow the ARB to assess the benefits of regulatory interventions with more specificity than is currently possible. This work can also increase understanding of specific source contributions to the mortality experience and of whether there are temporal patterns in the relative risks of mortality from air pollution. All of this information will strengthen efforts by ARB to implement policies that protect public health.

**BUDGET**: \$375,000 (potential cofunding from the South Coast Air Quality Management District to augment the budget.)

## TITLE: Improving Air Pollution Exposure Estimates in the Analysis of Mortality in the California Teachers Study Cohort

**PROBLEM:** Hundreds of studies implicate exposure to short-term ambient air pollution as a risk factor for exacerbation of pre-existing illness and for mortality in susceptible individuals. In contrast, much less is known about the health consequences associated with long-term exposures to air pollution and traffic. The effects associated with long-term exposure play an important role in determining annual ambient air quality standards and are a major factor in the calculation of health and economic benefits associated with air quality improvements. While few studies have examined relationships between long-term exposures and mortality, all have found positive associations with at least one pollutant metric; however, the results are not entirely consistent. In addition, significant uncertainties remain among these studies regarding the appropriate assumptions for exposure assessment.

**PREVIOUS WORK:** Researchers from the California Department of Health Services, the Office of Environmental Health Hazard Assessment, and the University of Southern California have embarked on an ARB-funded investigation of the California Teachers' Study (CTS), a prospective examination of the disease and mortality experience of over 100,000 current and former female public school teachers and administrators. Many members of this study population are at risk for developing and dying from cardiopulmonary diseases by virtue of their older age and post-menopausal status. To date, investigators have analyzed the relationships of long-term exposure to ozone on total and cardiopulmonary mortality, and anticipate completing basic analyses of the effects of exposure to several other pollutants and traffic metrics. As part of this effort, state-wide pollutant datasets dating back to at least 1988 have been created, including a historical reconstruction of PM2.5 developed under a related ARB contract.

**OBJECTIVE:** The objective is to examine the following research questions not addressed in the originally funded efforts: (1) What time period and duration of exposure (e.g., the most recent month or year, aggregation of the most recent three years, exposure from five to 10 years ago, and so forth) have the strongest associations with cardiopulmonary mortality? (2) What are the relative contributions of shorter-term versus longer-term exposures? (3) What are the impacts of varying distance assumptions when assigning exposures from fixed-site monitors or from GIS-generated traffic metrics? (4) What impacts, if any, do these alternative exposure metrics have on risk estimates for other outcomes not examined in the initial effort, such as cancer and nonmalignant respiratory disease? (5) Are associations altered when examining only never-smokers? (6) How are the effect estimates affected by alternative risk models that incorporate additional determinants of mortality, including ecological covariates? (7) Can any particularly susceptible subgroups be identified through stratified analysis? and (8) What do flexible modeling techniques, such as nonparametric smoothing, suggest regarding the shape(s) of the exposure-response functions?

**DESCRIPTION:** The current study team, under contract to ARB, is providing basic estimates of the effects of long-term exposure to PM10, PM2.5, ozone and other pollutant metrics on mortality and on the incidence of myocardial infarction and stroke. Investigators have developed initial estimates of exposure, linked to participants' geocoded residential addresses, that are more precise than those used in previous long-term cohort studies in

the U.S. However, this is a very rich data set which can and should be more fully explored this cohort does not have many of the confounders present in most other long-term studies of air pollution (i.e., these participants are all of the same gender, have similar levels of educational attainment, and have low smoking rates and [relative to other cohorts] low occupational respiratory exposures). Given the potential importance of the results of these analyses, it is crucial that multiple sensitivity analyses, which are not funded under the current agreement with ARB, be conducted. Uncertainties in exposure assessment are often raised by critics of studies such as this. Therefore, this issue will be explored and others that may affect the quantitative risk estimates, providing a full sense of the variability and reliability of these estimates.

**BENEFITS:** This effort would involve the analysis of existing datasets (including the health, pollution and traffic data) that have taken significant efforts to create, and would leverage the infrastructure of a large ongoing study. Since investigators have pollutant data for every month since 1988, the analysis would be the first to fully explore the relevant time periods of exposure to gaseous and particulate pollutants in relation to mortality outcomes, as well as the impacts of shorter- versus longer-term exposures. In addition, it is important to examine the sensitivity of the results to numerous alternative exposure assumptions. The results would be important in the next reviews of the ambient standards for particulate and gaseous pollutants in California and at the federal level, and may also affect quantitative estimates of the health and economic benefits of pollution control.

**COST:** \$225,000 (potential cofunding from the South Coast Air Quality Management District to augment the budget.)

## TITLE: Data Validation and Support of Continuous Monitoring at the Fresno Supersite as part of FACES

**PROBLEM:** Continuous and integrated measurements of particle size and chemistry are taken at the Fresno First Street monitoring station to evaluate new instrumentation, annual variability and trends, and health effects in conjunction with the Fresno Asthmatic Children's Environmental Study (FACES) conducted by the University of California, Berkeley. FACES was funded by the ARB as part of the ARB's multi-year efforts to establish clean air targets that protect the health of all Californian's, including sensitive individuals and those living in disadvantage communities. The FACES project will continue with National Institute of Health funding.

**PREVIOUS WORK:** The Fresno Supersite was established in 1999 by the California Air Resources Board (ARB) and the U.S. Environmental Protection Agency (EPA) to better understand the measurement, sources, and health effects of suspended particulate matter (PM). It served as the main anchor site for instrument evaluation as well as improvement and monitoring activities related to the Central California Regional PM10/PM2.5 Air Quality Study (CRPAQS) and the Central California Ozone Study (CCOS) through the winter of 2001. Since that time, data from the site has also supported the FACES project.

**OBJECTIVE:** The objectives is to provide Level 1A validated continuous data in CCAQS (Central California Air Quality Studies) format and submit to the CCAQS database and to the FACES investigators. The ARB's Monitoring and Laboratory Division has committed to provide continuing data support with basic, field-level, quality assurance.

**DESCRIPTION:** The following tasks will be performed to keep the Fresno Supersite in operation through December 2007 in order to assist ARB in researching the health and welfare effects of PM exposure and for evaluating long term particulate trends at the Fresno Supersite:

- 1. Provide Level 1A validated continuous data in CCAQS format and submit the validated data to the ARB's CCAQS database. As part of this task, DRI will:
  - a. Download and screen daily data and provide feedback and troubleshooting to the on-site technician for instrument failures.
  - b. Perform quality assurance, through Level 1A, on data from selected continuous instruments at the Fresno Supersite and other related studies. This validation includes the following steps: 1) verify instrument operation based on data and check sheets from field technician; 2) remove values for instrument downtime and performance tests; 3) make adjustments for calibration deviations; 4) plot data and review graphically; 5) investigate extreme values; 6) perform internal comparisons between collocated instruments; 7) assign appropriate data qualification flags; 8) when applicable, apply additional tests including jump tests and standard deviation test.
  - c. Convert the data to the CCAQS format and submit it to ARB withinsix months from the end of the sampling quarter.

2. Perform emergency instrument repair to supersite instruments. Emergency repairs will be coordinated with the on-site technician.

Other projects, such as the remaining U.S. EPA Supersite sponsorship, and internal DRI support will result in the following related tasks being completed:

- 3. Assist ARB with source characterization of data collected at the Fresno Supersite by analyzing new and archived Fresno filters and source samples by thermal desorption gas chromatographic mass spectrometry (TD-GC/MS).
- 4. Evaluate the size distribution of data including fine and ultrafine PM as well as coarse PM (PM10-PM2.5).
- 5. Evaluate new methods and technologies in continuous PM sampling.
- 6. Provide, as part of the data validation and analysis, presentations of results during project meetings
- 7. Publish results in peer-reviewed journals and cover page charges where applicable.
- 8. Visit to Fresno Supersite by Principal Investigator on a quarterly basis to identify if there are any deficiencies that need to be remedied.

**BENEFITS:** This project will provide validated data in coordination with the ARB MLD in support of the continuation of the FACES project. It will also provide the ARB with much needed validated data from Fresno that will be available for additional long-term studies in the San Joaquin Valley.

**COST:** \$150,000 (for Tasks 1 and 2) Tasks 3 through 8 will be completed with EPA and inhouse DRI cofunding in the context of other projects and internal research and development sponsorship

### TITLE: Relationship between Exposure to Ambient Air-Borne Particulate Matter and the Risk of Neurological Disease

**PROBLEM:** It is well-known that exposure to ambient levels of air-borne particulate matter (PM) can contribute to severe adverse health effects including asthma, lung diseases, cardiovascular disorders and cancer. However, much less attention has been paid to its influence on the central nervous system. Whether or not cumulative exposure to air pollution induces neural dysfunction, including progressive brain damage, is still poorly understood.

**PREVIOUS WORK:** In recent years there has been growing interest in the role of PM as a potential environmental factor in affecting cells of the central nervous system. based primarily on evidence from animal studies. For example, studies have demonstrated that ultrafine particles, a component of vehicular exhaust, could enter the brain through the olfactory-nerve pathway and cause inflammatory as well as other pathologies in aged rats (Obersdörster et al.; Elder et al., 2004). Also, Veronesi et al., (2005) found that when mice inhaled PM in concentrations that induced oxidative stress, dopaminergic cells of the central nervous system were affected. Specifically, they noticed that the cells of the substantia nigra compacta were reduced by 29 percent in those exposed to PM compared to uncontaminated air exposed control mice. Block et al. (2004) also examined the potential of particles, specifically diesel particles, to cause neurotoxicity and found that toxicity involved an oxidative process as well as phagocytosis. It has been hypothesized that even the cardiovascular effects that have been associated with ultrafine particles are in part due to the direct effects of ultrafine particles on the autonomic nervous system through sensory nerves in the respiratory tract (Oberdörster et al. 2005). While previous study point to a possible oxidant process, the specific mechanisms of neurotoxicity for ambient particles is unknown. Studies using animal and cellular models may offer new insight into the mechanism, while epidemiological investigation using existing databases may provide more information on the potential of air pollution to have measurable neurotoxicological effects.

**OBJECTIVE:** The objective is to study the effect of ambient particulate matter air pollution on the central nervous system.

**DESCRIPTION:** The specifics of the study have not been fully developed, however the study will likely be mainly toxicological, possibly using animal models or cell culture studies, or epidemiological in approach using existing databases.

**BENEFITS:** Completion of this project will contribute to understanding whether air pollution is associated with neurological diseases. If there is an association, this finding could contribute to setting limits for air pollution and thus significantly contribute to the overall health of Californians.

**COST:** \$400,000

### TITLE: Development and Use of a Mobile Facility for Animal Inhalation Studies to Particulate Matter from Various Sources

**PROBLEM:** The Southern California Particle Center (SCPC) has developed an impressive capability to address toxic particulate matter (PM) components and their adverse health effects. However, in spite of considerable progress in assessing aerosol samples, toxic components and mechanisms of injury, there has been apaucity of in vivo animal studies coming from Southern California, which is one of the most natural laboratories in the world to study PM adverse health effects. One of the major reasons for the inability to translate major in vitro discoveries about PM toxic components and biological mechanisms of injury into health effects is the lack of a state-of-the-art animal exposure facility. In particular, the contractor lacks a mobile PM collection and animal exposure facility that can be used to study PM health effects in conditions such as asthma and atherosclerosis. Currently, the SCPC has to make contractual arrangements with an investigator in Michigan to bring a mobile animal laboratory to Los Angeles for a limited number of weeks of the year. Otherwise SCPC investigators have to rely on an outdated transportable trailer that does not contain an animal vivarium or state-of-the-art PM exposure capabilities. Without access to a facility that can collect data at various locations and various seasons throughout the year, it is not possible to extrapolate seasonal, site-specific, source/receptor, and atmospheric data into in vivo health outcomes.

Numerous epidemiological and toxicological studies have found associations between measured PM mass and adverse health outcomes. However, prevailing scientific opinion asserts that, when considering plausible biological mechanisms of injury, PM mass is probably only a surrogate measure for other physical or chemical PM properties that form the actual basis for adverse health effect outcomes. An alternative approach to determine PM toxicity is to directly measure the relative toxic potential of PM from different sources, sites, and seasons, under real-world exposure conditions. While the potential sources of PM to the atmosphere may be numerous, the major contributors to PM mass at a given location usually number <10 (Schauer and Cass, 2000). A narrow the search is needed for critical chemical components by determining which PM sources are the most harmful under in vivo exposure conditions. This information will allow for more effective regulatory strategies with respect to source control, more targeted air quality standards, and ultimately, reductions in population exposure. Furthermore, once the most health relevant PM sources are identified, the list of hazardous particle characteristics can be narrowed down, thereby making more targeted mechanistic investigations of PM health effects possible.

**PREVIOUS WORK:** The U.S. EPA has recently awarded 5 PM centers, one of which is the SCPC. A major thrust of the SCPC activities is to determine the physical and chemical properties of PM emitted from different PM sources, including secondary formation, to evaluate how PM exposure and toxicity vary with respect to location, season, and particle size, and to assess their relative toxicity through *in vitro* studies. A major finding has been the demonstration of the role of oxidative stress and defining discrete biological stages of PM injury in tissue culture cells. Implementation of these findings to *in vivo* research is likely to define the basis of inflammatory injury and disease susceptibility in models such as asthma and atherosclerosis. However, due to

the focus on mechanistic studies, insufficient funds for *in vivo* research, and lack of animal exposure facilities, very limited animal inhalation exposure studies have been proposed by the SCPC. If, however, the scope of the animal studies can be expanded, the strength of the ongoing studies in the SCPC will be considerably augmented to the benefit of ARB, the EPA and the Particle Center.

**OBJECTIVE:** The objective is to develop a facility to conduct animal inhalation studies of various PM sources at a variety of different sites and during different seasons. The facility will be self-supported, including a vivarium, and deployed concurrently to the same field locations where *in vitro* PM sampling will be performed by the SCPC. The *in vivo* data will considerably strengthen *in vitro* mechanistic studies, including the elucidation of PM characteristics (e.g., size and composition), deposition, clearance and transport that cannot be addressed by *in vitro* toxicity studies. Advanced chemical analysis and source apportionment techniques will provide a quantitative characterization of the PM as well as the source contributions at each sampling site. In addition, state-of-the-art technologies will provide a method to measure the toxicity of PM components based on their chemistry and volatility

**DESCRIPTION**: The facility will consist of the exposure chambers for animal inhalation studies, a vivarium for animal storage, space for fine, coarse and ultrafine particle concentrators, an air sampling and monitoring unit and the pump and blower compartment. In addition, an array of state-of-the-art aerosol instrumentation will be deployed to provide detailed information about the physico-chemical characteristics of PM and co-pollutants during the exposure studies. All aerosol instruments, including the particle concentrators, are already available at the SCPC. Funds requested through this program will be used for the: (i) construction of the facility, (ii) personnel, (iii) administration to carry out the inhalation studies, as well as for (iv) the actual execution of *in-vivo* and *in-vitro* assessments. The entire facility will be enclosed in a trailer and will be transported, initially to USC and later to other locations within the greater Los Angeles basin, where there are marked differences in toxic air components. CARB will be asked to negotiate access to sites that they control in the Los Angeles basin and to make a facility available or rent a site at which the trailer can be parked when it is not in use. Inhalation exposure sites will be selected such that they are significantly influenced by the following PM sources: Diesel traffic; Gasoline traffic, including cold-start conditions; Secondary Formation; Road and Brake Dust; Aircraft and Airport Activities; Ships and Port Activities; Residential Wood Combustion.

Due to the time that it will take to construct and test the trailer, in the first two years of the program the animal studies will be limited to the assessment of (i) *ultrafine vs fine*, as well as (ii)*semivolatile vs non-volatile (refractory)* PM at the USC exposure site in downtown Los Angeles. The principal study model will be the investigation of atherosclerotic lesion development in genetically susceptible (e.g., ApoE and LDL-receptor knockout) mice. Depending on vehicle type, age and ambient conditions, between 70-90% of the particles by number and 10-30percent by mass may consist of more volatile materials than others. The exposure and health implications of these findings have not yet been investigated. Considering that the majority of people's exposure during commute will be dominated by these particles based on particle

number, it would be useful to know whether the non-volatile or semi-volatile material is more toxic.

Beyond the first two years of study, attention will be directed to animal exposures at alternative exposure sites such as: (i) The 710 (heavy duty) vs the 110 (light duty) freeways, or Caldecott tunnel, bores 1 vs 2: this will help to differentiate between the effects of gasoline and diesel particles; (ii) airport and seaport emissions will be sampled in the areas immediately downwind of the LAX airport and the harbor of San Pedro; (iii) inland receptor areas: samples heavily impacted by secondary particle formation, atmospheric aging and transport of toxic principles will be assessed at sites such as Riverside. Tests for the effect of season, temperature and relative humidity on particle formation and toxicity during winter and summer months at the same locations will also be conducted. For each sampling campaign, exposures to coarse, fine and ultrafine particle size ranges will be conducted separately. This will help to distinguish sources of PM (such as road dust) as well as to determine the most toxic particle size fractions. The proposed facility will also enable us to conduct for the first time both in vitro and in vivo CAP studies along well-defined air trajectories in the LA Basin during photochemical episodes, thereby making it possible to investigate the effects of atmospheric aging and secondary PM formation on PM toxicity. Towards that goal, the trailer will be deployed in 3 distinct areas in the LA Basin (i.e., a source, intermediate, receptor sites) over the course of the same day (3 hrs in each site) and animal inhalation as well as in vitro toxicity samples will be collected in each of these sites for several weeks during the photochemically active summer months.

**BENEFITS:** This project will provide much-needed insight into the source-exposureresponse continuum outlined by the National Research Council by developing fundamental understanding on the links between specific sources and in vivo adverse toxicological outcomes associated with exposure to PM. The information generated by this project will serve as the basis for linking emissions to local air quality and ultimately to health effects. These data on which PM sources are the most toxic, combined with detailed chemical and physical characterization of PM from these sources will allow for a narrower, more focused effort in identifying the biological mechanisms of PM health effects. This project affords considerable leveraging upon recently completed and ongoing EPA-funded Supersite and PM Center initiatives as well as ARB sponsored research. It could also attract funding from sources outside ARB to conduct complimentary studies.

**COST:** \$800,000 for the first two years of the project in order to get the trailer constructed and perform limited studies at the USC site. Beyond that, the work proposed at alternative locations and seasons will require \$800,000 support for years 3-4. The administration of the trailer will be done from the University of California, Los Angeles.

### TITLE: Satellite Measurements to Improve California's Models for Ozone and Particulate Matter

**PROBLEM:** Air quality models are traditionally limited to comparisons with data on an episode basis because of the high cost of the calculations and the data collection. Eight hour standards for ozone and PM based on seasonal exposures are not well served by the short duration emission inventories created for these episodes. In addition, communities directly exposed to primary pollutants in or near industrial and port areas are not always the same as those exposed to the secondary pollutants that traditionally are the metric by the models are evaluated. Further, most comparisons between model and data are focused on ozone and PM mass with considerably less attention (because the data is not as widely available) to the distribution of ozone precursors or to the composition of PM. This limits the accuracy of emissions inventories for NO<sub>x</sub>, VOC and particle precursors and results in a modeling system that is tuned to the locations where violations of state standards are currently most frequent-possibly at the expense of accurate predictive capabilities in regions that are not now in violation but might become so in the near future. Observations of total column NO<sub>2</sub>, CO, H2CO, CHOCHO and aerosol are now available in some cases with global daily coverage at resolution as small as 13x24 km. However, these data have mostly been used as constraints on global models examining continental scale emissions and they have seen little use in regional and urban air guality monitoring.

**PREVIOUS WORK:** There have been extensive efforts in making and obtaining measurements of nitrogen oxides for the purpose of improving the mechanisms that are the basis of air quality models and have been directly involved in efforts to use aircraft and ground based measurements to evaluate the retrieval of tropospheric NO<sub>2</sub> column amounts from the OMI and SCIAMACHY satellite based instruments. Researchers have performed 3-D modeling of the effects of climate on air quality in northern and central California (JGR submitted). Recently (GRL. in press), researchers have used measurements from SCIAMACHY to examine the detailed mechanism of NO<sub>x</sub> emissions associated with urea fertilizer, using the daily time resolution of the satellite measurements to compare to a process based mechanism. Work in progress shows that there is a strong correlation and near one to one correspondence between observations of NO<sub>2</sub> in California as collected by ARB and those from the SCIAMACHY satellite instrument.

**OBJECTIVE:** The objective is to develop the capability for routine application of inverse modeling techniques in combination with satellite measurements from SCIAMACHY and OMI to improving the retrospective and predictive capabilities of models applied to ozone. The initial product of this project will be a NO<sub>x</sub> emissions inventory for the time period 2003-2005 developed using NO<sub>2</sub> observations from SCIAMACHY and OMI as constraints. The new inventory will combine prior knowledge of the timing of emissions during each day with column amounts to produce an inventory that represents each month, with day of and day of week resolution. For example, there is a strong day of week difference of column NO<sub>2</sub> during a couple of months observation over northern California. Note that while the resolution of 13x24 km of the new OMI satellite is larger than the ideal, the grid spacing is higher resolution than one could typically achieve by interpolating between sites in the current observational network. Also, the pixels are not

exactly in the same location each day and the atmospheric transport patterns are not identical day to day providing further opportunity to achieve higher effective resolution through clever schemes for inversion of the observations. Subsequent research will include direct and simultaneous inversion of the NO<sub>2</sub>, H2CO, CO, CHOCHO and aerosol measurements that are now or can soon be expected to be available. Our inversion strategy will permit the chemical data to improve both the representation of sources and sinks in the model but also to directly feedback on the model transport.

**DESCRIPTION:** There will be a five year effort with the first two years devoted to deriving a complete annual  $NO_x$  emission inventory for the entire state and to developing capabilities for direct inverse modeling within the California domain. Subsequent years will be used to evaluate trends in  $NO_x$  emissions, to using the inverse model to understand the strengths and weakness of the model transport and chemistry and for extension to other species observed from space.

**BENEFITS:** This program will provide useful analyses of immediate value for use in air quality attainment strategies for 8-hour ozone and PM.

**COST:** \$350,000

## TITLE: A Universal Land Use Regression for Predicting Ambient Air Pollution Concentrations in California

**PROBLEM:** Accurate exposure assessment to air pollutants is one of the key challenges in environmental epidemiology. Many of the most common exposure assessment techniques have serious limitations. The expense of air monitoring, for example, generally precludes measurement at subject addresses, air dispersion modeling requires extensive (and often unavailable) data inputs, and kriging regional monitors fail to adequately capture small-scale variation such as the local effects of high-traffic intersections.

**PREVIOUS WORK:** Recent research has led to accurate local predictions using a procedure known as land use regression. In San Diego and Alameda County, California; New York City, New York; and Toronto, Montreal and Hamilton, Canada, it has been demonstrated that nitrogen dioxide *validation locations withheld from the modeling* can be predicted, on average, to within approximately 16 percent and that particulate matter (New York City) can be predicted to within 7 percent using solely a small set of monitors and geographic data on land use, population and traffic.

In addition to producing successful predictions in a variety of environments, recent efforts involving land use regression have uncovered significant consistency in both the strongest variables involved in the modeling and in their parameter values. This consistency in outcomes from different areas encourages explicit comparison of parameter values and the amount of variation explained by variables from region to region to assess the potential of a more "universal" model – one that could be adapted to local data availability and applied in areas with limited monitoring.

Comparisons involved nitrogen dioxide sampling in several locations at several different time periods. The San Diego data collected by the Environmental Health Investigations Branch in October 2003 was used as well as four sets of samples collected by the Environmental Health Investigations Branch (EHIB) or the Office of Environmental Health Hazard Assessment (OEHHA) in Alameda County (April 2002, May 2002, November 2004, and May 2005). Finally, nitrogen dioxide sampling conducted in and around New York City between 1999 and 2001 was included.

A set of seven consistently strong variables (total traffic, truck traffic, length of road, industrial land use, residential land use, total population and total housing units), that could be consistently measured at all locations ,were selected. For each of these seven variables, at each monitoring location, a GIS was used to calculate their values at five different buffer distances (40, 100, 300, 500, 1000 meters). Researchers then regressed each of these buffer/variable combinations against NO<sub>2</sub> levels for each set of samples. The parameter values, standard errors and variance explained were recorded and these results were analyzed themselves and included in a meta-analysis. It was determined that even though air dispersion patterns, sources of air pollutants and land use differ significantly from region to region, a comparison of land use regression results from San Diego; Alameda County, California; and New York City suggests that similar variables with similar parameter values predict nitrogen dioxide well.

Although the actual NO<sub>2</sub> values vary seasonally, these differences follow a consistent pattern and could be accounted for in a universal model. Researchers found that the EHIB monitoring in November, for example, tended to be approximately 6 ppb higher than the monitoring in May, but that the difference was consistent from monitor to monitor and did not vary substantially geographically. These results suggest that a universal land use regression model could be built using existing air monitoring data and could be used in epidemiologic research where monitoring data is unavailable.

**OBJECTIVE:** The objective is to develop a universal land use regression model for predicting NO<sub>2</sub> and PM2.5 concentrations for use in burden of illness and epidemiologic investigations across California.

**DESCRIPTION:** The California studies discussed above generally relied on geographically and temporally limited monitoring conducted by EHIB and OEHHA. The monitoring plans were specifically designed to answer epidemiologic questions and did not necessarily include a wide variety of different scales. Monitoring by the California Air Resources Board provides a unique combination of high numbers of monitors with a monitoring plan that covers a wide range of scales. With monitoring at the micro, middle, neighborhood, urban and regional scale and high numbers of monitors – more than 100 for NO<sub>2</sub> and approximately 75 PM2.5 monitors (in 2005) – ARB data would enable the implementation of large scale land use regression that could be applied statewide.

A calculation of the traffic and land use variables discussed above at all ARB monitoring sites for NO<sub>2</sub> and PM2.5. This would include total traffic, truck traffic, road length, industrial land use, residential land use, population and housing units at five different buffer distances. Then a land use regression model will be built using these variables to predict NO<sub>2</sub> and PM2.5. Next, investigators will cross-validate the universal model against the EHIB, OEHHA, and newly collected monitoring data collected as part of an ARB-funded project in Los Angeles. The local cross validations will be used to explore how well the universal model predicts in different urban areas of California and across seasons.

**BENEFITS:** After development, validation and peer review of the models, a data set that predicts small-area variations across all of California will be delivered. The original data will be posted on the ARB website for use by other investigators. Efor the cities and towns of state based on a 100 m lattice of points will be available. Original data will also be available for other investigators to calibrate specialized models for predicting exposures in epidemiological studies. This information will be used to enhance exposure profiles in numerous epidemiologic studies, may be linked to other information such as the California Health Information Survey, and will serve as a basis for exposure in burden of illness studies.

**COST**: \$250,000

## TITLE: Flux Measurements of Biogenic Precursors to Ozone and Particulate Matter in the Central Valley

**PROBLEM:** Ozone and aerosol simulations focused on the Central Valley are critical for State Implementation Plan development for ozone and particulate matter (PM). Model simulations are sensitive to emission sources, deposition/sinks, chemical reactions, and meteorology. Biogenic volatile organic compounds (BVOCs) participate in ozone and aerosol formation, and comprise a substantial fraction of ARB's VOC emission inventories. Also, as regulatory controls are extended to agriculture, there is a renewed focus on crop biogenic emissions. While inputs to the ARB's BVOC emission inventory model have been evaluated using field measurements, modeled emissions have not been evaluated using in-situ micrometeorological flux measurements for important valley floor crop environments. Enclosure and landscape-scale BVOC flux measurements are both critical for emission model performance evaluation, and for reducing uncertainties in emission inventories. In addition, recent field measurements suggest that fast reacting terpene species may be underestimated by 80 percent (Kurpius and Goldstein, 2003), and no measurements of emissions from crops are available to evaluate this potential emission for modeling purposes.

PREVIOUS WORK: The summer 2000 Central California Ozone Study, the California Regional Particulate Air Quality Study, and the 1990 San Joaquin Valley Air Quality Study focused on intensive monitoring of high pollution episodes. By design, these studies represent peak events rather than the range of ozone and PM climatology, and do not address emission inventory and emission model development. ARB sponsored several studies to identify critical data deficiencies in BVOC inventory development, and then proceeded to systematically address those needs. ARB-sponsored studies have included measuring branch-level BVOC emissions for selected plant species, developing leaf mass estimation methods for trees found in urban landscapes, developing leaf mass and leaf area data for oaks in natural landscapes, and validating vegetation maps and satellite-derived remote sensing land surface data in 35 locations in California. ARB BVOC emission model outputs have been evaluated using BVOC emission measurements from Blodgett Experimental Forest, an upper-elevation Ponderosa Pine plantation in the Sierra Nevada Mountain range, but no such measurements have been performed in dominant valley floor environments such as croplands.

**OBJECTIVE:** The objective is to use in-situ measurements of BVOC emissions, micrometeorology and atmospheric chemical reactions within selected agricultural landscapes over growing seasons to evaluate BVOC emission model performance and improve the representation of emissions and atmospheric processes. Crops cultivated on the valley floor likely comprise a large source of monoterpenes, sesquiterpenes, and other compounds, but their emission potentials have not been measured extensively, and no measurements have been made with the most modern equipment available today. Enclosure measurements from a range of crop plants that are prominent in the valley, followed by canopy scale measurements at several sites would comprise a focused evaluation of biogenic emission potential from crops suitable for advancing emission inventory models.

Specific objectives include:

- (1) High frequency, continuous, micrometeorological and enclosure-based techniques will be used to measure BVOC emissions, ozone deposition, ambient VOCs, and atmospheric chemical reactions above selected agricultural landscapes. Techniques include gas chromatography, proton-transfer reaction mass spectroscopy (PTR-MS), eddy covariance and relaxed eddy accumulation. Measurements will also permit the speciation of monoterpenes and oxygenated VOCs emitted by crops, of which little is known.
- (2) Measure atmospheric concentrations of biogenic chemicals and their oxidation products at multiple sites. Locations will provide opportunities to measure ozone and PM precursor exchange with dominant lower elevation and valley floor crops.

**DESCRIPTION:** A phased two-year field study is proposed. In the first year, BVOC emissions at the branch or whole plant scale will be characterized for key crops that dominate farming practices in the valley. From these data, two sites will be selected from which to conduct landscape-scale, micrometeorological BVOC flux measurements on the most critical crop types based on emission potential and landscape coverage data. In the second year, landscape-scale flux measurements will be performed at two selected sites. Vegetation metrics utilized in BVOC emission models (plant species composition and dominance, canopy area, leaf area index, leaf mass density, etc.) will be collected simultaneous with the measurements. Continuous ambient speciated hydrocarbon measurements during the field campaigns will also be used to assess the anthropogenic and biogenic contribution to total observed VOCs, at different times of the day, at the selected locations.

An extensive set of chemicals will be measured at each site including ozone, CO, and hydrocarbons including biogenic and anthropogenic compounds, and speciated aldehydes and ketones. Chemical species and micrometeorological variables will be measured continuously at high temporal resolution (tens of minutes, hourly).

Observations will describe temporally and spatially varying emission rates and chemical processes for important Central Valley agricultural landscapes, and as functions of vegetation community composition, growing season, and meteorological conditions. Measured landscape-scale BVOC emission rates from crops will be used for developing needed emission models for dominant agricultural crops. Further analyses may permit development of emission algorithms for less well understood but abundant Oxygenated Volitile Organic Compound (OVOCs), such as oxygenated compounds. Measurements of oxygenated species will provide additional means for evaluating chemical processes leading to ozone and PM formation.

**BENEFITS:** This project will provide useful data for BVOC emission model evaluation and development, and will help reduce uncertainty in BVOC emission inventories for the Central Valley. Data analyses can test underlying air quality modeling assumptions regarding emission inventories and oxidation of fast reacting biogenic compounds.

**COST**: \$400,000

## TITLE: Deployment of a Novel Aerosol Mobility/Mass Spectrometer for Quantitative Chemical Analysis of Organic Aerosols from Mobile Sources

**PROBLEM:** Understanding the physiological mechanisms responsible for the observed correlations between particulate matter and morbidity and mortality requires better instrumentation for in-situ characterization of ambient aerosol. In general, real-time instrumentation, volatility, and hygroscopicity, are reasonably well-established. By contrast, real-time chemical analysis of aerosols is a relatively young field that only began taking shape in the late 1990s with the development of laser ablation-based single-particle mass spectrometers. Presently, deployable methods for aerosol chemical analysis fall short of providing the quantitative and comprehensive speciation data that may be obtained through filter extraction in the lab. This is especially true for organic molecules, which tend to fragment upon particle laser ablation, or electron beam ionization of the molecules desorbed from the particle. This is unfortunate since semi-volatile organics present in the condensed phase may only be definitively analyzed in situ. Thus there is a need for an instrument that can quantitatively identify the organic content of fine and ultrafine particles.

PREVIOUS WORK: Historically, chemical analysis of particulate matter involves drawing an aerosol sample through a filter, or using an inertial impactor to sample aerosol particles in a size-selective manner. Such methods are still in use today since they provide the most comprehensive and quantitative chemical information. Two major drawbacks of these so-called bulk techniques are that they provide data that are temporally averaged over a long sampling period (typically hours), and that important volatile or semi-volatile organic species are lost from the substrate prior to analysis. The need for rapid chemical analysis of aerosol particles led to the development of singleparticle mass spectrometers, including PALMS (Murphy and coworkers), ATOFMS (Prather and coworkers), and RSMS-II (Wexler and coworkers). These instruments are all deployable and have been used to acquire a large amount data from field experiments. Despite a lack of quantitation afforded by such instruments due to size and composition biases inherent to the one-step ablation/ionization process, these instruments represent the only way to analyze individual fine and ultrafine aerosol particles in real time. The current archetype for quantitative analysis of particle ensembles is the Aerodyne AMS instrument, which has been included in countless field campaigns around the world within the last five years. A beneficial feature of the AMS, compared to single-particle instruments, is its ability to provide quantitative mass data for non-refractory chemical species. However, even the AMS suffers from fragmentation of organics due to the relatively hard ionization induced by the electron beam. The purpose of the instrument deployment proposed here is to provide supplementary in-situ quantitative analysis targeting intact organic molecules present within the fine and ultrafine size fractions of the ambient aerosol. Thus the focus here is on soft ionization of the parent molecules, and subsequent measurement of molecular shape as well as mass, in order to facilitate a more definitive identification.

**OBJECTIVE:** The objective is to deploy the aerosol mobility/mass spectrometer in collaboration with ongoing field measurements through the Southern California PM

Center. The deployment will target light and heavy duty freeways, the Los Angeles shipping port, and LAX airport.

**DESCRIPTION**: The proposed work applies the deployment of novel instrumentation in order to gain a better understanding of the formation, evolution, and health effects of organic aerosols in the Los Angeles basin. The instrument combines the well-established methods of electrostatic aerosol classification, thermal desorption/chemical ionization, and ion mobility/mass spectrometry. The latter has not yet been applied to analysis of aerosols, but is commonly used for analysis of large biological molecules. The primary goal of the proposed instrument design is to provide an additional means for compound identification, in series with the high-resolution mass spectrometer. In this case, the mobility of the desorbed ions through a counterflow of a drift gas will be determined in addition to the mass of the ions. The instrument operates as follows. Ambient aerosol is passed through a conventional Polonium-210 neutralizer to provide the aerosol with an equilibrium charge distribution. The aerosol is then forced through a critical orifice and into a low-pressure electrostatic classifier that collects essentially mono-sized particles onto a heating element for subsequent thermal desorption.

The size of the collected aerosol depends on the applied voltage and may vary between 10 nanometers and several hundred nanometers in diameter. The desorbed molecules are carried by a Nitrogen sheath flow into a chemical ionization region, where a radioactive source (most likely Am-241) initiates the gas phase ionization reactions. The gas phase positive ion chemistry is actually driven by the trace amount water present in the flow leading to H+(H2O)n ions and a clustering reactions. These ions are robust, long-lived, and low-energy species. These newly formed ions are gated into an ion mobility drift cell, allowing for mobility separation of the ions. A fraction of the ions are allowed to pass through a pinhole at the end of the drift cell, and are focused into a high-resolution orthogonal-extraction reflectron mass spectrometer (lonwerks Inc., Houston), allowing for a time-of-flight mass spectrum of the ions. The resulting data set will provide a size-resolved, chemically-speciated, and quantitative description of the aerosol in real time. The instrument may also resolve volatility of the compounds if the temperature of heating element is ramped slowly. The instrument has been designed, and is now nearing completion. It will be completed and calibrated under EPA funding, so this ARB proposal focuses exclusively on the field deployment of the instrument in collaboration with the Southern California PM center at the University of Southern California.

One of the more interesting recent observations within the Los Angeles basin is the existence of a highly concentrated ultrafine aerosol immediately downwind of both lightduty vehicle [Kuhn *et al.*, 2005] and heavy-duty vehicle [Zhu *et al.*, 2002] freeways. The concentration appears to decrease sharply with downwind distance, suggesting that the particles are evaporating, rather than coagulating [Zhang *et al.*, 2004]. This makes insitu analysis the only viable option for determining the chemical composition of these organic particles, which may pose a health risk to those who live near freeways [Zhu *et al.*, 2005]. A similar observation has recently been made in the vicinity of LAX, where peak concentrations in excess of 600,000 particles/cm3 were observed by two condensation particle counters [Biswas *et al.*, 2005]. These peaks correspond to aircraft landings and far exceed the peak concentrations observed near freeways. Since this is a new result, no chemical analysis is available yet, but it is clear from the excessive concentrations that further scrutiny into the chemistry and potential health effects associated with these events is warranted.

**BENEFITS:** Aerosol mobility/mass spectrometry represents the only way to identify and quanitify organic compounds in fine and ultrafine aerosols in situ. Such composition measurements can be correlated with *in vivo* and *in vitro* toxicity experiments in order to understand the health effects of aerosols emitted from mobile sources. This is especially relevant to those who live in the vicinity of freeways, shipping ports, and airports. The resulting data sets on organic aerosols from mobile sources will aid in urban airshed model development. Successful deployment of the instrument will also result in new methodology for future investigations of indoor air pollution, global radiative effects of aerosols, and cloud formation, focusing on organics.

**COST: \$**240,000

# TITLE: Characterization of Source-Specific Contributions to Air Pollution by Measurements of Isotope Ratios and Marker Compounds

**PROBLEM:** Elevated levels of pollutants in ambient air can increase adverse health effects such as mortality, cancer, and hospital admission and consequently take a significant toll in Californians' lives. To obtain cleaner air quality, pollutant loads need to be significantly curtailed by restricting emissions especially from anthropogenic sources. It is important to know the contribution of pollutants from different sources to the total burden of ambient air pollution in order to develop efficient management strategies. Though many studies investigated sources of pollutants using numerous tools such as source-specific markers and isotopic signatures, few have combined these tools as cross validation techniques.

**PREVIOUS WORK:** Carbon isotope ratio (C14/C12) has been successfully applied to determine the contribution of fossil fuels to the burden of atmospheric particulate matter and a specific class of pollutants such as polycyclic aromatic hydrocarbons (Bench et al., 2004). Source-specific marker compounds such as levoglucosan and cholesterol, and benzothiazole also have been used for source apportionment (Kleeman et al., 1999). One study conducted in Japan measured carbon isotopes in size-resolved particles (Endo et al., 2004). This study found higher fraction of modern carbon than expected in fine particles (<1.1  $\mu$ m). Carbon isotope ratios in different fractions of PM (water-soluble and water-insoluble organic carbon and elemental carbon) have not been measured.

**OBJECTIVE:** The objective is to identify the contribution of fossil fuel combustion, wood burning, meat cooking, and natural direct input to the burden of size-resolved carbonaceous PM and volatile organic compounds (VOCs).

**DESCRIPTION:** Field samples will be collected to investigate the geographical differences and temporal changes in contribution of pollutant sources. Sampling will take place at two urban sites (Los Angeles and Fresno) and one remote site for a year. Bulk particles (PM10) and VOCs will be collected once a month. Separation of PM10 into three fractions (e.g., water-soluble and water-insoluble organic carbon and elemental carbon) for isotope measurement will be conducted every two months. Size-resolved particles will be collected four times to measure isotope ratios and marker compounds. Compound-specific isotope ratios of polycyclic aromatic hydrocarbons in bulk particles will be measured four times to investigate seasonal variation.

Studies of isotope analysis of PM from remote and suburban sites in the summer (assume little home fireplace use) found Carbon-14 levels very near contemporary biogenic material, suggesting that the majority of particle mass is from biogenic sources. In the absence of forest fires, living trees/plants must be out-gassing compounds that are sorbed onto particles. It is unknown whether the particles collected are strictly fossil vs. biogenic carbon or a small fossil core with a biogenic coating. The fossil core formed during combustion will not be particularly volatile while the biogenic coating was deposited in the aerosol phase. Separate volatile and non-volatile components of size-

resolved PM from each site will be used to test the hypothesis that fossil nanoparticles are serving as nucleation sites for the generation of PM. These data can provide information regarding sources and particle growth mechanisms.

Carbon 14 measurement can distinguish PM from fossil fuels versus all other contemporary carbon sources such as wood burning, meat cooking, and direct emission from plants and animals. The contribution of each contemporary carbon source to the total burden of carbons will be determined using source-specific markers. Levoglucosan and cholesterol will be used to identify the contribution of PM from wood burning and meat charbroiling, respectively. Compound-specific isotope measurement can provide accurate information regarding sources of pollutants such as polycyclic aromatic hydrocarbons. As a supplementary work, benzothiazoles (tire-specific markers) will also be measured to quantify the contribution of tires to atmospheric PM and trace metals such as zinc especially in urban areas (Reddy and Quinn, 1997). Carbon 14 measurements will be conducted using accelerated mass spectrometry (AMS) at Lawrence Livermore National Lab. Concentrations of levoglucosan will be determined using a gas chromatograph equipped with a mass selective detector (GC-MS).

**BENEFITS:** The data collected will significantly reduce uncertainties associated with estimating PM and VOC emission inventories from indirect measurements and assist in validating models. More accurate information will allow the state of California to develop more efficient air quality control strategies and management options.

**COST:** \$427,000

#### TITLE: Assessing Near-Field Exposures from Distributed Combustion Sources

**PROBLEM**: Much air pollution exposure is caused by pollutant release from distributed combustion sources that emit in close proximity to people. Examples include motor vehicles (gasoline and diesel), fireplaces, and off-road diesel engines. Near-field exposures, defined here to be those occurring within 100 m of the source, are not well characterized by routine monitoring data, since monitoring sites are selected to be away from the direct influence sources. Yet people are often quite close to these sources and time spent in proximity may contribute significantly to the total exposure burden. For developing effective policies that mitigate excessive exposures, the near-field exposure burden must be quantified. Gaussian plume models are ineffective in the near field, and models based on computational fluid dynamics are expensive and unproven as near-field exposure-assessment tools.

**PREVIOUS WORK:** The concept of intake fraction was developed in recent years to quantify the source-to receptor relationship for emission sources. It has been used to characterize cumulative population exposure to major ambient sources, such as primary motor vehicle emissions and combustion-based, electricity generation units. The metric has also been applied to study the self-pollution of school buses owing to the entrainment of exhaust. In this case, the near-field exposure of children constituted a major portion of the overall exposure impact of the buses. Several studies have also characterized pollutant concentrations owing to motor vehicles in the near vicinity of roadways. With a few possible exceptions, these studies have not characterized the source-to-receptor relationship in a way that facilitates generalizing from the particular circumstances of each study. Intake fractions from indoor releases have also been assessed. Overall, major gaps remain in our understanding of near-field exposure impacts across the array of potentially important sources.

**OBJECTIVE:** The objective is to characterize the near-field components of intake fraction attributable to certain important distributed combustion sources. In doing so, improve the base of knowledge for assessing the near-field exposure impacts of sources that emit close to people.

**DESCRIPTION:** Experiments will be conducted using sulfur hexafluoride or another suitable tracer gas. The basic experimental approach entails controlled release of the tracer gas over a short period (~ minute) from a source of interest. An array of pump-and-bag samplers will be deployed to collect time-integrated air samples in the near-field region around the source. This experiment would include both indoor measurements and outdoor measurements as appropriate. So, for example, to investigate residential wood combustion, the tracer gas would be released into the chimney of an operating fireplace and measure tracer gas concentrations in that home, plus in the homes of nearby residents. The incremental intake fraction associated with each monitoring site would be estimated by (mass collected/mass released)  $\times$  (air volume breathed by occupants during sampling period/air volume sampled). The total near-field intake fraction would be determined by summing the contributions for all near-field exposures. Seventy-five experiments (total) would be conducted investigating three source classes, to be selected by the researchers in consultation with ARB. Sources

could include motor vehicle emissions in a street canyon, residential wood smoke, and a distributed electricity generation unit in an urban area.

**BENEFITS:** This project would generate important new data quantifying near-field exposures as consequence of important combustion processes that occur close to people. The results would illuminate the importance of the near-field effect as a component of the overall exposure burden of major air pollution sources. To the extent that the near-field exposures are important, the results would inform efforts to prioritize control strategies so as to efficiently minimize exposures. The results would also be important in informing environmental justice concerns owing to the near proximity of certain population groups to air pollution sources.

### TITLE: An Observational Investigation of Offshore Ship Emissions of CO, $NO_X$ , and $SO_X$ from Continuous Observations at a Coastal Site

**PROBLEM:** Carbon monoxide (CO) is a trace gas of immense importance in mediating the oxidative capacity of the background atmosphere.  $NO_X$  is central to atmospheric chemistry because it too modulates ozone and free radical abundances.  $SO_X$  is an important precursor to aerosols, and emissions from ship traffic have been minimal. Because of the inherent non-linearity of atmospheric photochemistry and transport, the initial conditions of any air quality model are extremely important to the accuracy of the results. In order to accurately predict air quality throughout California and efficiently regulate pollution sources, it is necessary to better understand the nature and magnitude of emissions of these compounds from the coastal oceans directly upwind of our domain.

**PREVIOUS WORK**: Recently, ship emissions have been identified as having the potential to affect air quality in many high traffic coastal regions [Corbett & Fischbeck, 1997; Capaldo et al., 1999]. Initial observations of continuous, high-rate CO concentrations made by our group at Bodega Bay have indicated considerable onshore advection of pollutant plumes from coastal shipping traffic. While efforts have been made to quantify offshore emissions of NO<sub>x</sub> and SO<sub>x</sub> using bottom-up estimates of fuel consumption and vessel activity, many uncertainties in these techniques persist [Corbett & Koehler, 2003], and there has been few, if any, direct observational support for the estimates. Furthermore, unpublished data from Professor Kleeman's group at the University of California, Davis indicate a substantial amount of sulfate aerosols at Bodega Bay.

**OBJECTIVE:** The proposed project is aimed at supporting continued and expanded monitoring operations at Bodega Bay for the purpose of quantifying emissions of CO,  $NO_x$ , and  $SO_x$  from offshore shipping channels. Careful analysis of the dimensions and sum of these pollutant plumes will help characterize the regional pollutant sources from offshore shipping.

**DESCRIPTION:** Investigators will operate a one second CO instrument at Bodega Bay, but to augment the research station with commercial trace level instruments modified for improved sensitivity and temporal resolution and establish bulk statistics of this compound's onshore flux. Moreover, after establishing the amounts of these compounds contained in the spikes above background levels, investigators will scale them and compare them to the ratios expected from standard diesel emission indices. Also their cumulative emissions can be quantified and compared to available emission inventories. Shipping traffic data will be collected to carefully inventory the expected emissions for comparison with observed values.

**BENEFITS:** The proposed work will provide a very sound, observationally based estimate of the magnitude of marine shipping sources, which have traditionally not been included in air quality models. This data analysis will allow for an improved understanding of the background state of our atmospheric environment, and will consequently improve our ability to most efficiently regulate terrestrial sources. These activities are in direct alignment with the key research priorities of CARB in improving

emission inventories, in this case in the context of the complex and highly trafficked coastal environment. The work therefore benefits Californians by paving the way for effective protection of their prodigious natural resources, as well as their agricultural and health standards.

# TITLE: Laboratory and Field Studies of the Atmospheric Chemistry of Aromatic and Polycyclic Aromatic Compounds and the Role of NO<sub>2</sub> in their Product Distributions

**PROBLEM:** Aromatic and polycyclic aromatic compounds (PACs) are emitted from combustion sources such as vehicle exhaust. Many aromatic hydrocarbons and PACs, as well as their atmospheric transformation products, are known to be toxic and/or carcinogenic. Risk assessments must consider the health implications of both the directly emitted aromatics and their products produced in the atmosphere. Presently the details of the atmospherically important hydroxyl (OH) radical-initiated reactions of aromatics and PACs are not well understood. Key guestions remain concerning the NO<sub>2</sub> concentrations at which the OH-aromatic and OH-PAC adducts react dominantly with NO<sub>2</sub> versus dominantly with oxygen and how this affects the products produced. While it appears that the OH-monocyclic aromatic adducts react with oxygen under atmospheric conditions, to date glyoxal and methylglyoxal yields have mostly been obtained at elevated NO<sub>2</sub> concentrations and data are needed at realistic ambient NO<sub>2</sub> concentrations. Whether the OH-PAC adducts react with oxygen or with NO<sub>2</sub> in the atmosphere is presently not known and this has implications for formation of nitro-PACs from PACs. A more complete understanding of the processes controlling nitro-PAC formation in the atmosphere is required before the impact of changes in NO<sub>x</sub> emissions on nitro-PAC formation can be reliably assessed.

**PREVIOUS WORK:** Researchers at Air Pollution Research Center at the University of California, Riverside have made significant contributions to the current status of knowledge of aromatic and PAC atmospheric chemistry. They have previously shown the importance of ambient nitro-PAC formation from radical-initiated atmospheric reactions and that the isomers formed from these reactions are often distinct from those nitro-PAC in direct emissions. Solid phase micro-extraction (SPME) techniques and gas chromatography/mass spectrometry (GC/MS) have recently been used to identify dicarbonyls formed from the OH radical reactions with both monocyclic aromatic hydrocarbons and alkylnaphthalenes. The proposed work is an extension of CARB-funded research, which will provide a more complete picture of the products formed from atmospheric reactions of monocyclic aromatic hydrocarbons and their yields and the formation routes to nitro-PACs in the atmosphere and the role of NO<sub>2</sub> in their formation.

#### **OBJECTIVES:** The objectives of the project are to:

- 1) Elucidate the formation mechanisms of nitro-PACs in the atmosphere by studying in the laboratory the formation of nitro-PAC from the radical-initiated reactions of PACs as a function of NO<sub>2</sub> and verify the mechanisms through ambient sampling of PACs and nitro-PACs.
- 2) Determine the glyoxal and methylglyoxal formation yields under atmospheric conditions for the OH radical-initiated reactions of toluene, the xylenes and the trimethylbenzenes, by measuring their yields in the laboratory as a function of NO<sub>2</sub> concentration.

**DESCRIPTION:** Recent developments using Solid Phase Microextraction (with and without on-fiber derivatization) sampling in combination with positive and negative chemical ionization GC/MS analysis have resulted in improved sensitivity for nitro-PACs and the ability to quantify glyoxal and methylglyoxal as their oxime derivatives. It is anticipated that SPME sampling techniques combined with negative ion chemical ionization GC/MS analysis will allow rapid nitro-PAC identification and quantification as a function of NO<sub>2</sub>. Therefore, investigators will use a large-volume environmental chambers to: (a) investigate the formation of nitronaphthalenes and nitrobiphenyls from the OH radical-initiated reactions of naphthalene and biphenyl as a function of NO<sub>2</sub> concentration and (b) to measure glyoxal and methyglyoxal formation yields from a series of monocyclic aromatic hydrocarbons as a function of NO<sub>2</sub> concentration.

Field studies measuring nitro-aromatics (*m*-nitrotoluene, nitronaphthalenes, methylnitronaphthalenes, 3-nitrobiphenyl, 2-nitrofluoranthene and 2-nitropyrene, and potentially 2- and 3-nitrobenzanthrone and nitrotriphenylenes) and their aromatic precursors will be conducted at selected locations and times. If the laboratory studies show different involvement of NO<sub>2</sub> in the reaction pathways of monocyclic aromatics in comparison with the PACs, ambient measurements should confirm these differences. Analyses will be made by GC/MS utilizing well-established procedures. Negative ion chemical ionization will be employed to provide the requisite sensitivity for the nitro-PAC analyses.

**BENEFITS:** Elucidation of the formation mechanism for nitro-PACs will allow a better understanding of the impact of control strategies for  $NO_x$  emissions on the ambient formation of toxic nitro-PACs. Knowledge of the products and their yields from the atmospherically important reactions of monocyclic aromatic hydrocarbons will improve computer models for predicting urban and regional ozone pollution.

**COST:** \$300,000

### TITLE: On-Road Motor Vehicle Emissions Measurements including Ammonia and Sulfur Dioxide

**PROBLEM:** There is very little information on ammonia emissions from real vehicles on the road. Ammonia is a major component of airborne PM2.5 and there are few other ammonia sources in the LA basin. Dynamometer studies at the University of California, Riverside have shown that ammonia emissions vary with load and with the tier of emission control. Sulfur dioxide emissions, especially from diesel vehicles, are a potential indicator of misfueling.

**PREVIOUS WORK:** There has been one published study of on-road ammonia emissions measured by means of on-road remote sensing (Baum et al 2000) which observed a relatively small number of vehicles. Researchers have now developed a UV based on-road remote emissions sensor which reliably gives not only carbon monoxide (CO), hydro-carbon (HC), carbon dioxide (CO<sub>2</sub>) and nitric oxide (NO) fuel-based mass emissions readings from passing light duty vehicles but also provides the same quality of data for ammonia and sulfur dioxide. An emission inventory for the LA basin about to be published by Huai et al. predicts that ammonia emissions are currently dominated by the ammonia emissions from older cars measured only in a single 1993 tunnel study (Fraser and Cass 1998).

**OBJECTIVE:** The objective is to monitor all the above pollutants from approximately 60,000 light duty vehicles, 20,000 each in three regions of California, the Los Angeles basin, the central valley and the Bay area. The results, when combined with fuel sales data, will provide a fuel-based emission inventory, and will investigate if there are any differences between the three regions in terms of emissions and in terms of potential misfueling.

**DESCRIPTION:** The FEAT 3000 is the University of Denver's routine on-road emissions monitor. It has been used in California for the IMRC in 1999 at several sites, and for the CRC every two years at a single site, the intersection of LaBrea Blvd. and I-10 in Los Angeles. The instrumentation and the normally available data including speed and acceleration and vehicle make and model year are fully described in CRC E-23 reports available on the web at <u>www.feat.biochem.du.edu</u>. The new features which have been added include new optics and a wider UV detector array which allow SO<sub>2</sub> and NH3 to be monitored simultaneously with the routine pollutants. This development was described by Burgard et al at the April 2005 Coordinating Research Council (CRC) Meeting in San Diego. It is possible to include a unit which monitors NO<sub>2</sub> along with CO, HC and CO<sub>2</sub> if ARB decides that on-road NO<sub>2</sub> emissions would be a desirable addition.

In operation, a mobile van sits at the roadside during daylight hours for about one week at each location. Returns to the La Brea site in LA, returns to the IMRC interchange ramp (101N to 880N) in San Jose and a suitably chosen site in the central valley. The techniques or research methods to be employed are identical to those used in two recent studies in the Denver area and in Tulsa OK which will be reported at CRC 2006 in San Diego by Burgard et al. Other than the addition of the two new pollutant channels they are identical to those used in the CRC E-23 studies.

Tasks to be achieved include location of a suitable central valley site, apply to California Department of Transportation for permits for all sites, ensure that all calibration gases are available and certified by appropriate authorities, carry out the studies, read license plates, match plates for make and model year with California Department of Motor Vehicles and report the findings.

**BENEFITS:** New knowledge of the current mobile-source ammonia and sulfur dioxide emissions inventory. An indication as to whether these emissions vary from region to region within California.

**COST:** \$95,000 (additional funds are required to include the addition of  $NO_2$  capability is useful, or there is a desire to add the same study goals but applied to HDDV emissions.)

### TITLE: Secondary Port Truck Activity Study

**PROBLEM:** The Ports of Los Angeles and Long Beach are together the third largest container port in the world. Every day at these ports freight is transferred from oceangoing vessels to trucks and rail facilities for overland transport. Containers may be transported from ocean-going vessels to on-dock rail directly, or transported by local dravage (port) trucks to near- or off-dock rail facilities. These splits were used for development of the port truck emissions inventory for the Goods Movement Emissions Reduction Plan (GMERP). For the GMERP, ARB staff estimated the fraction of containers moved by truck regionally versus outside of the South Coast region or outside of California. Some of these containers were assumed to be transloaded (repackaged from 2 TEU to 3 TEU containers. The fact that a large portion of containers (35-50% of all inbound containers) are likely handled by a distribution center for truck transport either locally within the South Coast or regionally to out of state destinations is important, and implies significant truck activity at distribution centers. Almost nothing is known about these secondary truck trips, such as where these truck trips are generated, where these truck trips terminate, what types of trucks perform these trips, and what fraction of total truck emissions at these centers are generated by movement of international (import and export) goods in California. This study would answer these questions.

ARB is beginning a process to evaluate the potential impacts of distribution centers. This study could augment the Board's effort by providing additional data and documentation to help identify distribution centers that service international containers and estimate activity from trucks, transportation refrigeration units, and cargo handling equipment that operate these facilities.

**PREVIOUS WORK:** The Ports of Los Angeles and Long Beach developed baseline emissions inventories in 2004, representing truck emissions within terminals, on port property, and outside of the port out to South Coast Air Quality Management District boundaries in the base year 2001. The process of updating these emissions inventories has just started and will be completed in 2006. In 2005-2006, ARB staff developed an emissions inventory representing secondary truck trips related to international goods movement for the Goods Movement Emissions Reduction Plan, which was developed from data generated by the Southern California Association of Governments, the Ports, and other agencies.

While these studies have been effective in estimating vehicle miles traveled (VMT) associated with secondary truck trips, they were not designed to assess emissions associated with the transfer of goods at distribution centers, and the potential localized impacts which may be caused by Particulate Matter (PM) emissions in areas such as the Inland Empire where distribution centers are located.

**OBJECTIVE:** The objective of this research will be to characterize the fleet of trucks that make secondary trips related to the movement of international containerized goods in the South Coast, identify distribution center facilities that service these containerized goods, and quantify emissions associated with those truck trips, and activity of trucks and other equipment operating at distribution centers.

**DESCRIPTION:** This research will identify distribution centers that service local and regional container movements by truck, including truck and rail transloads. A survey will be conducted that identifies inbound and outbound trip origin, destination, and vehicle characteristics of trucks servicing a representative sample of these distribution centers; and a second survey will be conducted to identify on-facility truck, TRU, cargo handling, and other equipment emissions at each surveyed facility. Survey data will be used to estimate emissions associated with secondary trips and emissions associated with distribution centers servicing the ports of Los Angeles and Long Beach. A report will be generated summarizing these results and highlighting potential methods for emissions reduction.

Specific tasks are estimated as follows:

- 1. Conduct an origin/destination survey of trucks servicing the ports of Los Angeles and Long Beach to identify distribution centers to which containers would be delivered.
- 2. Select a geographically and trip-representative sample of distribution centers for further study.
- 3. Conduct an origin/destination survey of trucks entering and exiting each distribution center. Include vehicle characteristics in survey.
- 4. Conduct a survey of truck, transport refrigeration unit, and cargo handling equipment activity at each distribution center.
- 5. Estimate emissions and health risk at each surveyed distribution center.
- 6. Extrapolate emissions from sampled to non-sampled distribution centers to estimate total activity and emissions.
- 7. Estimate VMT and emissions associated with secondary international container truck trips in California.
- 8. Develop a final report summarizing results.

**BENEFITS:** Evaluating secondary port truck trips would improve the Board's understanding of the impact of goods movement emissions on the statewide inventory as a whole. Studying these impacts would also improve the Board's- understanding of the community-level impacts of distribution centers on local air quality. Ultimately, a greater understanding of secondary port truck trips will lead to development of improved emissions models and control strategies to meet air quality goals.

# TITLE: Development of the UCB Particle Monitor for California Applications in Epidemiology and Environmental Justice

**PROBLEM:** Although epidemiological studies using Particulate Matter (PM) measurements at ambient monitoring stations routinely show consistent effects for important health endpoints, there is also recognition that actual human exposures sometimes differ substantially in temporal and spatial distribution from what these stations show. To better understand the relationship of particle exposures and ill-health and to better target control measures to address exposure, there is need for technologies to monitor particle levels in a wide range of locations, preferably with high temporal resolution. In addition, there is a need for particle monitors simple, rugged, reliable, and inexpensive enough for use by community groups interested in environmental justice and other applications.

**PREVIOUS WORK:** Currently, there are ambient station technologies, however, are not up to these tasks, principally because of capital cost, but also because they tend to require frequent attention by highly trained technicians and special housing for protection from the elements and security. Moving such devices around by truck only addresses part of the need for characterizing particle levels in space and time and cannot do so economically over large areas and long time spans.

There are smaller and cheaper instruments available, generally designed for the occupational market, that could partly fill this need. One class of such devices relies on light-scattering chambers combined with data logging, to give high temporal resolution. These devices are fairly robust, although they are not designed for continuous long-term unattended deployment. As with any light-scattering device, there are some limitations in their ability to accurately determine particle mass, but the principal constraint still remains cost and need for attention. Their retail cost is about \$4,000 each at present and even if purchased in large numbers, the likely per unit cost still makes them prohibitively expensive for most applications. Their durability in this intended use is also questionable, largely because they must rely on a pump to draw air through a size-cut device. Such pumps require field calibration, and the most durable ones currently cost several hundred dollars each and necessitate connection to power lines.

**OBJECTIVE:** The objective is to adapt and test a low-cost datalogging particle monitor using commercial smoke-alarm sensors developed by the University of California, Berkeley (UCB) for third-world use in California conditions 1) to facilitate measurements by community environmental justice groups and large-scale particle epidemiologic studies, 2) monitor high-particle environments such as street canyons, wood-burning neighborhoods, and vegetation fire events, and 3) improve its capabilities to monitor real time particle size distribution at typical California ambient levels.

**DESCRIPTION:** UCB has developed and tested a small, smart, fast, and cheap particle monitor, called the UCB monitor. They have built about two hundred and have been using them for more than 2 years in a number of developing countries in their research and as part of training for non-research community pollution work. As part of this project they will extend its utility to three categories of applications in California The three categories of applications in California will be:

1) <u>Environmental justice and epidemiologic applications</u> requiring good temporal and spatial resolution of PM changes, but not requiring highly accurate estimates of absolute mass concentrations below 50  $\mu$ g/m<sup>3</sup>:

2) <u>High particle environments</u> (>50  $\mu$ g/m<sup>3</sup> PM2.5): Although annual mean outdoor levels of PM in California are will below 50  $\mu$ g/m<sup>3</sup> PM2.5, there are important micro-environments with higher levels. These include

- vehicle tunnels and street canyons,
- neighborhoods with strong sources, e.g., wood-burning fireplaces/stoves,
- indoor locations with environmental tobacco smoke or other particles from indoor sources,
- vegetation (forest, grass, crop waste) fire plumes.

An additional application could be as an emissions monitor for such sources as fireplaces, woodstoves, and other relatively low-temperature small-scale combustion devices.

Based on the past extensive development of the UCB for third-world high-particle environments, the contractor could fairly directly develop models that would meet most of the criteria above for determining absolute concentrations at high temporal and spatial resolution in such high-particle settings in California. The choice of which settings would depend on ARB priorities.

The current device would require relatively little further sensor and electronic development to be tested in these applications, of course in conjunction with standard devices for validation. New cases, power arrangements, wireless communication technology, and data handling/analysis methods could also be developed for these applications.

- 3) <u>Development of advanced capabilities</u>: To be able to reliably measure
- absolute mass concentrations below 50 μg/m<sup>3</sup>,
- particle number,
- continuous PM size distribution.

**BENEFITS:** Low-cost easy to deploy monitoring technologies continues to be of high interest, particularly with respect to characterizing community exposure. This project will provide a monitor that is small, quiet, micro-power battery-operated for non-intrusiveness, easily placed, capable of long deployment, low maintenance, and inexpensive so that it can be operated in various environments. The monitor would be capable of providing data that is timely, manageable, and accurate for PM2.5 and below.

**COST:** \$250,000 (potential cofunding from the California Energy Commission to augment the budget)

# TITLE: Evaluation of Existing Air Pollution Control Technologies for Use in Controlling Exhaust Emissions from Ocean-Going Vessels at Sea

**PROBLEM:** The exhaust from ocean-going vessels (OGVs) contains high levels of particulate matter (PM), nitrogen oxides ( $NO_X$ ) and sulfur oxides ( $SO_X$ ). These emissions impact California's onshore air quality, particularly for communities near major ports and shipping lanes. While the impacts of OGV emissions are significant, there are few OGVs with emission control devices because they are subject to relatively little air pollution control. In addition, the use of emission controls on OGVs is constrained by the limited space onboard vessels, and the use of high sulfur fuels that deactivates some catalysts.

**PREVIOUS WORK:** Existing technology has been refined for many years to control the emissions used on stationary power plants and most mobile sources. At least in theory, many of these technologies can be used to control emissions from OGVs. For example, the large diesel engines used to propel OGVs are very similar in design to diesel engines used in many stationary power plants, and in some cases they burn similar heavy fuel oils. Therefore, the more advanced control equipment on stationary power plants could be used to control OGV engines if practical constraints can be overcome. One manufacturer (Advanced Cleanup Technologies, Inc.) is currently constructing a system that attempts to adapt existing control equipment to marine and locomotive applications. The system, called AMECS (Advanced Maritime Emissions Control System) and a similar one called ALECS (Advanced Locomotive Emissions Control System), utilizes existing scrubber technology and selective catalytic reduction technology adapted for locomotive and marine applications. This system is designed to remove a substantial amount of PM, SO<sub>X</sub>, and NO<sub>X</sub>, and is scheduled to be tested on locomotive engines in July, 2006, at the Roseville Railyard, then relocated to control emissions from marine auxiliary engines at the Port of Long Beach. If successful, this system may be a candidate for controlling emissions from the larger propulsion engines on OGVs. Another system referred to as a "seawater scrubber" is manufactured by a Canadian company (Marine Exhaust Solutions). This system is designed to reduce SO<sub>X</sub> and PM emissions, and is currently being tested in sea trials. Another technology that has been used in some marine and stationary power plant applications is water/fuel emulsions, which controls peak combustion chamber temperatures and NO<sub>X</sub>.

**OBJECTIVE:** The objective is to identify the most promising emission control technologies for OGVs considering all possible technologies, especially those not currently used on marine vessels. The ultimate goal is to incorporate these technologies on OGVs to reduce PM,  $SO_X$ , and  $NO_X$  emissions.

**DESCRIPTION:** Under the proposed research project, the contractor will review the full spectrum of existing emission control technologies for large diesel engines, regardless of current application, and evaluate their potential for use in controlling OGV emissions at sea. The advantages and disadvantages of each technology will be discussed, along with a description of the cost, pollutants controlled, manufacturers of the technology and current applications (marine or non-marine). A special emphasis will be placed on controls that are not currently used in marine applications, such as those used on stationary power plants. The potential to incorporate technologies on OGVs as retrofits,

as well as incorporating them in new vessel designs will be considered. This contract is considered to be an initial step, with the intention that subsequent contracts would specify the development of detailed engineering drawings and designs that could be used to incorporate the most promising control technologies in actual vessels (either as retrofits or new builds). A final step would be the actual construction and emissions testing of the systems.

**BENEFITS:** Successful completion of this contract will help to focus future emission control projects for OGVs on the most promising control technologies for reducing PM,  $SO_X$ , and  $NO_X$ , and may identify some new possibilities previously overlooked.

### TITLE: Update ARB's Solvent Cleaning Emissions Inventory

**PROBLEM:** Solvent cleaning is one of the top five non-mobile sources of volatile organic compound (VOC) emissions in California. However, ARB's current solvent cleaning emissions inventory is based on data that are more than ten years old and no longer reflect current technology. During the past ten years, the types of solvents being used have changed significantly, due to the designation of acetone as an exempt compound, the banning of ozone-depleting substances, and changes in regulations. Many districts need to update their solvent cleaning rules to obtain additional VOC emission reductions and meet State Implementation Plan (SIP) commitments, but they don't have the up-to-date inventory information that is needed to accurately calculate those reductions. In addition, solvent cleaning is often conducted by small businesses that do not have air permits and are located near residential areas, particularly in environmental justice communities. ARB needs improved data, including speciation profiles, to assess exposure in these communities. ARB also needs more accurate information and speciation profiles to pursue innovative approaches for achieving additional emission reductions, such as reactivity-based measures.

**PREVIOUS WORK:** At the 14th Annual Emission Inventory Conference, a paper was presented titled "Solvent Mass Balance Approach For Estimating VOC Emissions From Eleven NonPoint Solvent Source Categories" by D.L. Jones, et.al. This paper focuses on national regulations and it directs states/local agencies to assess the effects of local regulations. In California, the Department of Toxic Substances Control and the Institute for Research and Technical Assistance (IRTA) have performed some field studies to convert businesses to low-VOC solvents, but these studies are not extensive enough to provide the data that is needed to update the statewide inventory.

**OBJECTIVE:** The objective is to update ARB's solvent cleaning emissions inventory and speciation profiles to reflect current solvent cleaning materials and technologies.

**DESCRIPTION:** Complete the following activities:

- Conduct field surveys for a variety of businesses that conduct solvent cleaning.
- Identify the types and quantities of solvent cleaning materials being used and the associated technology employed (e.g. heated dip tanks, ultrasonic units, enclosed power washers, vapor degreasers, hand-wipe cleaning, etc.)
- Develop emission factors for the various solvent cleaning technologies, including speciation of the ingredients contained in the solvent cleaning materials.
- Update ARB's statewide emissions inventory and speciation profiles for solvent cleaning.

**BENEFITS:** This project will provide information that can be used to identify additional opportunities to achieve VOC emission reductions from solvent cleaning operations, thereby improving air quality. It will also provide ARB with the ability to update the solvent cleaning emissions inventory to reflect changes in photochemical reactivity and toxicity, which in turn allows ARB to better assess the impact of solvent cleaning emissions on communities.

**COST:** \$200,000

### TITLE: An Assessment of Emissions from the Use of Biodiesel as a Motor Vehicle Fuel in California

**PROBLEM:** The Legislature passed Assembly Bill 1007 (AB 1007) that requires the Air Resources Board (ARB) and the California Energy Commission to develop a plan to increase the use of alternative fuels in California. Alternative fuels can reduce California's dependence on imported oil and reduce air pollution. Also, the Governor established aggressive greenhouse emission reduction targets for which the ARB has identified potential emission reduction strategies using alternative fuels such as biodiesel. Biodiesel is an alternative diesel fuel that has the potential to reduce greenhouse gas emissions, other pollutants, and can reduce our use of petroleumbased fuels. However, knowledge gaps exist and further research is needed in characterizing the impact biodiesel has on oxides of nitrogen emissions, the effect various feedstocks have on emissions, and the effect biodiesel has on emissions from on-road and off-road diesel engines. This research is needed to facilitate biodiesel lifecycle analyses and to determine the potential benefits and disbenefits of biodiesel. This research would also assist in the development of biodiesel fuel specifications, if necessary.

**PREVIOUS WORK:** The U.S. EPA published a draft technical report that evaluates the impact of biodiesel on pre-1997 engines. Most of the studies cited in the report were on soy based biodiesel and its effect on criteria pollutants. A U.S. EPA Tier 1 emissions study on criteria and toxic emissions and a tier 2 health effects study were conducted as part of the US EPA fuel registration process. Again, these studies were limited to soy based biodiesel. Also, a Montreal transit bus study evaluated both criteria and toxic emissions. National Renewable Energy Laboratory (NREL) is currently conducting a study on newer engines. Most of these studies are limited in their direct application to California because soy based biodiesel may not be the major feedstock used in California and because exhaust emissions from diesel engines fueled with biodiesel were not compared to engines fueled with CARB diesel.

**OBJECTIVE:** The objective of the proposed biodiesel research is to fill knowledge gaps to provide the necessary data to facilitate life cycle assessments needed for programs implementing greenhouse gas emissions reductions and the evaluations required under AB1007.

**DESCRIPTION:** The proposed research would evaluate biodiesel blends (B5 and greater) and neat biodiesel (B100). Low blend levels would likely represent a reasonable economic and technical scenario where biodiesel could be mass marketed in California in the near future. Higher biodiesel blends and B100 would represent possible niche markets or broader scenarios in later years when domestic production has matured. Research would be conducted to evaluate biodiesel feedstock emission impacts from on-road and off-road post-1997 engines and engines with aftertreatment. A key area of research would be on the impact biodiesel use has on NOx emissions.

Three biodiesel feedstocks would be used for the study. Emissions testing would be conducted on heavy-duty chassis and engine dynamometers. A limited number of onroad and off-road engines and vehicles would be tested. This could include current model engines, 2007 compliant engines, and a hybrid vehicle. It may be possible to collaborate with NREL, since NREL is conducting a B20 study on new technology engines. This would allow the incorporation of engines and B20, a blend of biodiesel that is gaining national acceptance, into this study. This would be accomplished by testing a limited number of additional engines using B4 at NREL in exchange for testing an equal number of engines using B20 in our evaluation. Since B20 is a well-studied fuel, it would serve as a biodiesel baseline as well as a reference for comparison to other studies.

Also, this study would benefit from participating with the College of Engineering –Center for Environmental Research and Technology (CE-CERT) because of their expertise in biodiesel emissions testing and state of the art testing facility. Incorporating CE-CERT into this study could be accomplished by providing additional monetary funds to augment current programs focused on emissions studies on on-road engines using biodiesel. Off-road testing would be conducted at ARB's Stockton test laboratory.

Chemical analysis and limited biological testing would be conducted. Chemical species include greenhouse gases, criteria pollutants, toxic air contaminants, and reactive organics. Specific classes of compounds would include aromatics, hydrocarbons, carbonyl compounds, inorganic and organic chlorine compounds, and metals. Fuels analysis would also be conducted to evaluate the need for biodiesel fuel specifications such as for stability, cold flow, and other key parameters. Some of the toxic analyses would be conducted by ARB.

**BENEFITS:** Californians would benefit because this study would help ARB programs by quantifying the air quality and greenhouse impacts of biodiesel that would in turn help in developing a plan for alternative fuel use in CA. This would ultimately reduce our dependence on petroleum-based fuels, improve air quality, and aid in mitigating our waste disposal problem.

**COST:** \$350,000 (ARB is seeking additional funds for this project to increase the budget to \$650,000)

### TITLE: Engine Lubricating Oil Impacts on Mobile Source PM Emissions

**PROBLEM:** Engine lubricating oil is a significant contributor to the formation of mobile source particulate matter (PM) emissions, including nanoparticle emissions. This is true of engines burning gasoline, diesel fuel, and natural gas. As fuels become cleaner and emission control systems become more effective and durable, the contribution of the lubricant becomes increasingly significant. Studies have shown that high PM-emitting engines (oil burners) are the most toxic in terms of potency per unit mass of emitted material.

**PREVIOUS WORK:** Toxicity studies have concluded that lubricant-derived PM yields a mutagenic response. The Gasoline/Diesel PM Split Study has demonstrated that PM from spark-ignition vehicles is a significant contributor to ambient PM levels in the SoCAB, but the exact role of lubricating oil on normal and high-emitting vehicles of various technologies has not been resolved. Recognizing this knowledge gap and the potential benefits to air quality and human health, the National Renewable Energy Laboratory (NREL), South Coast Air Quality Management District (SCAQMD), and the California Air Resources Board (ARB) have expressed mutual interest in a study to characterize the potential for reformulated lubricants to reduce PM emissions from inuse mobile sources, both from new vehicles and from the much larger in-use vehicle fleet (by using reformulated lubricants in old vehicles). As a first step and at the request of CARB, NREL wrote a white paper that summarized recent literature on the role of lube oil on engine emissions, and the paper has been reviewed by ARB and SCAQMD staff. The document summarizes results from previous studies and describes a program plan to investigate the role of lubricating oil on vehicle emissions. The following is a summary of the major findings and recommendations from this literature review that are detailed more fully in the white paper:

- The literature suggests that various lubricant properties affect PM emissions. The strongest correlations with PM are lubricant volatility and ash content.
- Synthetic lube oils (poly-alpha olefin, PAO) yield lower PM emissions as well as improved fuel economy.
- The age of the engine oil (miles since oil change) may have a significant impact on PM emissions, as certain combustion byproducts are entrained in the lube oil and eventually emitted along with the lube oil in the particle phase.
- The mechanisms by which lubricant impacts PM are clearly different in sparkignited engines and in diesel engines. A test plan should be mindful of this difference.
- Especially in spark-ignited engines, the selection of test cycle is critically important for "normal" emitters, PM emissions tend to be limited to cold starts, rapid accelerations, and high speed events.
- Test temperature appears to have a significant influence on emissions, with the highest PM levels emitted during cold-cold start conditions (especially in spark-ignited engines).
- PM emission rates and associated health effects tend to be significantly different in "high-emitters". A test plan should include newer vehicles as well as the

malmaintained "smokers" that may contribute disproportionately to emission inventories.

• Careful attention should be given to chemical speciation of the measured exhaust and the parent materials (fuel and lubricant). The selected test methods should be evaluated in terms of the potential for artifact formation or loss of exhaust PM, especially when unusually long sampling times are used.

**OBJECTIVES:** The objectives are to characterize the significance of lube oil in PM formation and to determine whether lube oil can be formulated to reduce in-use PM emissions from mobile sources, if it is demonstrated that lube oil is the largest contributor to PM from mobile sources.

#### **DESCRIPTION:** Investigators will:

- Chemically and physically characterize the PM emissions (including ultrafine particles) from gasoline, diesel, and CNG vehicles under a variety of scenarios (30°F and 72°F under a variety of engine operating conditions, including off-cycle operations), to understand/evaluate the source(s) of the PM and to understand whether the PM is derived from fuel, lube oil, or engine wear;
- Provided that lube oil is the most important source of PM, through chemical analysis attempt to understand the source of that PM from the lube oil;
- Work with engine oil and additive companies to formulate variety of fluids that do not include precursors to particle formation; and
- Perform additional emissions testing on same type of fleet of SI and CI vehicles to see whether PM can be reduced.

**BENEFITS:** Studies from California have shown that directly-emitted PM from mobile sources may be the most significant single contributor to ambient fine PM levels. Reformulated lubricating oils may provide a significant PM emissions benefit to new and existing vehicles under a variety of operating conditions.

#### **COST:** \$100,000 for CARB

This project represents co-funding from a consortium of sponsors: Department of Energy, National Renewable Energy Laboratory (\$200,000), and the South Coast Air Quality Management District (\$100,000) and the California Energy Commission (\$100,000).

#### TITLE: Diesel Engine Crankcase Blow-By and Diesel High PM Emitters: Determination of Contributions to Ambient Particulate Matter and Potential Health Effects

**PROBLEM:** Diesel engine crankcase blow-by is a ubiquitous source of diesel engine (DE) Particulate Matter (PM) emissions since nearly all heavy-duty diesel engines are equipped with 'road draft tubes' that vent crankcase emissions directly to the atmosphere. DE crankcase blow-by is estimated to account for up to ten percent (or more) of the total PM contribution from current DEs, but DE crankcase emissions have not been routinely measured because of a lack of test procedures. If this ten percent value is correct, then on a per-vehicle basis, DE crankcase blow-by emissions could rival the emissions contribution from high PM emitting light-duty gasoline vehicles (LDGVs, ~50-300 mg/mile). DE high PM emitters are recognized to exist, but to date have not received the same scrutiny accorded to light-duty gasoline vehicle (LDGV) high PM emitters.

Chemical Mass Balance (CMB) modeling results from the National Renewable Energy Laboratory (NREL) "gas-diesel split" project (2005) appear to indicate that smoking light-duty gasoline vehicles (LDGVs) could be significant contributors to ambient PM in the South Coast Air Basin (SoCAB). However, source profiles from neither DE crankcase blow-by emissions nor DE high PM emitters were included in this project. There is reason to suspect that DE high PM emitters and DE blow-by may chemically resemble LDGV high PM emitters (i.e., have lots of organic carbon), and hence the CMB results could be "mis-attributing" all of this organic carbon OC to LDGVs. Combined with the observation that on-road and off-road DEs are estimated to account for about 73 percent of the mobile source PM emissions inventory in the SoCAB (this figure rises to about 84 percent if two-stroke gasoline engines are included), this raises questions regarding veracity of these results since this suggests that a very small number of high PM emitting LDGVs overwhelm the much larger emissions contribution estimated to be from DE (and gasoline two-stroke) emissions sources.

In addition to their impact on the air burden for any particular region, there is also reason to suspect that diesel engine crankcase blow-by may be particularly toxic since used engine oil is known to cause adverse health effects (e.g., skin cancer in mice), and crankcase blow-by is essentially lubricating oil vapors. High PM emitting LDGVs and high PM emitting light- and medium duty diesel engines have both been shown to cause adverse health effects, but this has not been systematically studied for high PM emitting heavy-heavy-duty diesel engines (HHDDEs), and not for HHDDE crankcase blow-by.

**PREVIOUS WORK:** In September 2003, the Donaldson Company, Inc. obtained a US EPA Environmental Technologies Verification (ETV) Program verification for their Series 6100 Diesel Oxidation Catalyst Muffler and Spiracle Closed Crankcase Filtration System for HHDDEs. In demonstrating the emissions reduction potential for the Spiracle Filtration System, the emissions data set revealed that the baseline (uncontrolled) crankcase emissions were between 16-23 percent as great as hot start exhaust PM emissions under engine dynamometer FTP test cycle conditions. In the context of the Coordinating Research Council (CRC) project E-66, the principal investigator has

estimated that crankcase blow-by could account for up to 10 percent or more of the PM emissions contribution from in-use HHDDEs.

Previous SoCAB and San Joaquin Valley CMB studies (Schauer, et al., 1996, 2000) indicate that diesel engines could be the major mobile source PM contributors, while the Northern Front Range Air Quality Study indicated that LDGVs could be the major mobile source contributors in Denver, Colorado. The recently completed NREL "gas-diesel split" project indicated that LDGVs could be the largest mobile source PM contributor in the SoCAB, or that diesel engines could be the major source contributor (i.e., the two methods used in the study produced conflicting results, which are themselves in conflict with results from previous studies). The LDGV and LD-MD diesel vehicle toxicity study by Seagrave et al. (2002), indicated that high PM emitting gasoline and diesel vehicles have increased toxicity compared to either normally emitting gasoline or normally emitting diesel vehicles.

**OBJECTIVE:** The objective are to determine the influence of diesel engine blow-by and high PM emitter source profiles on CMB modeling results and investigate the toxicity of these emissions. These data could also be used to update the heavy-heavy-duty diesel engine/vehicle emissions inventory to include blow-by and high PM emitters.

**DESCRIPTION:** A test fleet of in-use heavy-heavy-duty diesel trucks (HHDDTs) would be procured and chassis dynamometer emissions tested over a variety of driving cycles, including the ARB 5-mode HHDDT test cycle and the HDV UDDS. The test fleet would include old, high mileage, high PM emitting HHDDTs, late model, high PM emitting HHDDTs, and late model, low PM emitting HHDDTs. High PM emitters would include both engines that are being mis-fueled, as well as engines that are burning oil. Both tailpipe as well as crankcase emissions would be sampled. Gaseous, semi-volatile, and PM emissions samples would be collected for subsequent detailed chemical analyses. CMB modeling runs would then be performed utilizing these new source profiles, and compared against the recent CMB results for the SoCAB. Toxicity would be inferred based on the speciation profiles. In addition to sample collection for immediate chemical analyses, additional samples would be collected that would be archived for possible toxicity analyses should the chemical speciation results indicate the further health effects (i.e., toxicity) studies are warranted.

**BENEFITS:** The results of this project would provide a more complete picture of the emissions contribution of these not-well-characterized, but potentially important, PM emissions sources. The results from this project could also shed light on the gasoline versus diesel PM emissions contribution question.

# TITLE: Life Cycle Analysis of the California Air Resources Board's Climate Change Reduction Strategies

**PROBLEM:** The State of California has a stated goal of reducing greenhouse gas (GHG) emissions, which cause global warming. The targets for reductions are to return to 2000 emission levels by 2010, 1990 levels by 2020, and 20 percent of 1990 levels by 2050 (i.e., an 80% reduction from 1990 levels). The blueprint for meeting the goals for 2010 and 2020 has been presented in a recent report by Climate Action Team (CAT) to the Governor. The report contains two tables listing individual strategies and their expected GHG emission reductions. The first table (Table 5-1, pages 36-37) contains strategies already under way, such as those being established by the Pavley bill (AB1493), strategies that are already well developed. The second table (Table 5-2, pages 41-42) contains additional strategies necessary to meet the reduction targets. These strategies have only recently been identified, and have not yet been fully developed. The second table includes nine additional strategies that will need to be fully developed by ARB. These nine strategies need to be further evaluated before they can be implemented. ARB staff has estimated the technical feasibility and expected emission reductions of these proposed strategies. However, further analysis needs to be performed to determine the life cycle emissions of the proposed strategies. For example, the use of a low-GWP (global warming potential) refrigerant will reduce overall global warming in the first instance simply because each unit of emitted gas will warm the planet less. It is however possible that the use of such a refrigerant would require new equipment that is more energy intensive to produce, and hence overall global warming reductions will be less than first calculated. These types of life cycle issues have not yet been resolved.

**PREVIOUS WORK**: ARB staff has developed 'workplans' for each of these strategies as they were developed to be included in the above mentioned CAT report to the Governor. The 2-5 page workplans contain further detail and a description of the strategy and the assumptions made in the emission reduction strategies. No work has been done so far to calculate the life cycle global warming emissions.

**OBJECTIVE:** The objective is to develop an algorithm for quantifying the life cycle emission effects of any measure that ARB staff may propose to meet the California GHG emission-reduction goals.

**DESCRIPTION:** First, the proposed project will need to include an extensive literature review of currently available methodologies and models to determine life cycle global warming emissions. Second any improvements deemed necessary must be made to current methodologies for calculating life cycle emissions.

**BENEFITS:** At the end of the project, the State will have a current model for calculating life cycle emissions that can be used in future work to meet the California global warming emission reduction goals.

#### **COST:** \$200,000

# TITLE: Improving the California Inventory for HFC Use and Emissions from Commercial Refrigeration

**PROBLEM:** The State of California has a stated goal of reducing greenhouse gas (GHG) emissions which cause global warming. The targets for reductions are to return to 2000 emission levels by 2010, 1990 levels by 2020, and 20 percent of 1990 levels by 2050 (i.e., an 80 percent reduction from 1990 levels). An important element in reaching these reductions is reducing HFC emissions from commercial refrigeration.

HFC's used in refrigeration are potent GHGs, with global warming potentials ranging from 140 to 3,800. These refrigerants are used in commercial refrigeration in increasingly large quantities as substitutes for ozone-depleting substances (mainly CFCs) that are being phased out in accordance with the Montreal Protocol. As such they have become a significant component of the overall GHG emissions in California.

Commercial refrigeration has been identified as the second largest emitter of HFCs from refrigeration and air conditioning in the United States by the US EPA. However, very little is known about the extent of use and emissions in California specifically. In order to quantify the California-specific HFC emissions from commercial refrigeration, additional work is needed to create inventories. This includes quantifying the populations of commercial systems by the type of HFC, the application, the emissions rate, the technical feasibility and cost of using low-Global Warming Potention (GWP) refrigerants, and the rate of turnover of these systems. Once these inventories have been completed, the State is in a position to tailor a specific strategy to reduce emissions from these sources.

**PREVIOUS WORK:** ARB staff is not aware of any "bottom up" California-specific work that has been done to quantify the use and emissions from commercial refrigeration. The US EPA has developed a model, The Vintaging Model, which estimates the use and emissions nationally. Unfortunately the model cannot be used to infer California specific-emissions and is essentially a 'black box'. The model relies on unpublished information that has been classified as 'Confidential Business Information', or CBI. Inquiries into the inputs to this model are unavailable as "public disclosure of the inputs to the Vintaging Model would jeopardize the security of the CBI that has been entrusted to the EPA."

**OBJECTIVE:** The objective of the project will be to quantify the populations of commercial systems by the type of HFC used, the application, the emissions rate, and the turnover rate to develop a baseline inventory for California. A secondary objective will be to quantify possible emissions reductions from such populations, may it be through leak reductions or from using low-GWP refrigerants.

**DESCRIPTION:** The proposed project would develop a detailed bottom-up inventory for commercial refrigeration, concentrating on retail food refrigeration. ARB will be seeking a methodology to assemble this inventory. It will have to include an assembly of current

knowledge, including gathering information from the EPA, trade groups and associations. It is possible surveying of existing facilities will be needed as well.

**BENEFITS:** The development of these inventories is necessary to improvement and subsequent development of reduction strategies for GHG emissions from commercial refrigeration.

### TITLE: Emissions of HFC-134a from Auto Dismantling and Recycling

**PROBLEM:** U.S. EPA regulations require that any HFC-134a remaining in the vehicle's air conditioning system be removed and recycled prior to vehicle dismantling at wrecking yards. However, there is anecdotal evidence which suggests that recovery does not occur in accordance with EPA's regulations. EPA does not aggressively enforce these regulations, and some auto wreckers have told the ARB staff that there is almost no market for the recovered HFC-134a or readily available person or operation to accept HFC-134a that is removed. As a result, the staff suspects that much of this refrigerant is not recovered and is emitted to the air during auto-wrecking operations. The extent to which HFC-134a is recovered in accordance with EPA regulations, and hence the emissions, is unknown. Because these so-called "end-of-life" emissions can negate some or all of the benefits of regulations which reduce servicing-related emissions, and in order to assess the feasibility of regulations which would be applicable to the auto dismantling industry, it is essential to have accurate estimates of end-of-life emissions.

**PREVIOUS WORK:** ARB staff conducted a small survey of auto wreckers in 2004 to estimate the amount of HFC-134a recovered during vehicle dismantling. The responses to this survey were very limited. In addition, the quality of the survey data was in some cases suspect. A more comprehensive survey or study is needed to better assess the extent of "end-of-life" emissions.

**OBJECTIVE:** The objective of this study would be to obtain an accurate estimate of "end-of-life" emissions of HFC-134a which occur when vehicles are dismantled.

**DESCRIPTION:** The most likely approach for obtaining the necessary emission estimates would be to conduct a comprehensive survey of HFC-134a recovery practices at auto dismantlers, possibly in cooperation with the auto dismantler's trade association (California Auto Dismantler's Association). Included in this survey would be a requirement that auto dismantlers provide to the ARB data on the amount of HFC-134a remaining in each car that passes through their operations.

**BENEFITS:** An accurate estimate of "end-of-life" HFC-134a emissions would allow an accurate assessment of the effectiveness and feasibility of regulations designed to reduce HFC-134a emissions during servicing operations and of regulations designed to reduce emissions from auto dismantling operations.

#### TITLE: HFC-134a Refrigerant Use by Non-Light-Duty Vehicles

**PROBLEM:** Motor vehicles use HFC-134 as the working refrigerant in their air conditioning systems. As part of the support for the climate-change regulations adopted by the Board in 2005, the ARB staff estimated the emissions of HFC-134a from light-duty vehicle air conditioning systems in California. The staff has not attempted to estimate HFC emissions from other categories of vehicles, for which there is little information available. To support any new regulatory proposals to reduce emissions of HFCs from all motor vehicles in California, estimates are needed for the emissions of HFC-134a from vehicles other than light-duty vehicles.

**PREVIOUS WORK:** The U.S. EPA has estimated national emissions of HFC-134a from all motor vehicles (including non-light duty) air conditioning systems, but these estimates were made using a proprietary model that is not accessible (free of substantial cost) to the ARB staff. Thus, the inputs, assumptions, and calculation methodology used in the model can not be independently verified and modified to produce emission estimates specific to California. Also, it isn't clear that vehicle categories (i.e., light, medium, heavy) can be disaggregated within the model to estimate emissions by category.

**OBJECTIVE:** The objective of this project would be to develop an emissions inventory of HFC-134a from non-light duty motor vehicle air conditioning systems. Ideally, the emission estimates would be broken down into several vehicle categories (medium-duty vehicles, heavy-duty vehicles, transit buses, etc.)

**DESCRIPTION:** There are probably a few ways to develop the necessary emission estimates. One approach would be to survey heavy-duty truck operators (possibly by way of the California Trucking Association) on the frequencies air conditioning system recharges and the amounts refrigerant recharged. A representative survey sample would permit extrapolation to the entire heavy-duty vehicle population. Transit buses could be similarly surveyed. It is possible that the emission estimates could be made also by surveying the producers and distributors of the HFC-134a, who might have data on how much refrigerant is distributed to shops that service heavy-duty vehicle air conditioning systems.

**BENEFITS:** This project would provide estimates of emissions of HFC-134a from air conditioning systems on vehicles other than light-duty vehicles. Such estimates are needed to estimate the possible emission reductions.

#### TITLE: Evaluation of the Potential Impact of Emissions of HFC-134a from Non-Professional Servicing of Motor Vehicle Air Conditioning Systems

**PROBLEM:** In order to save money, many individuals choose not to have their vehicle's air conditioning (AC) system serviced by professional, certified automotive air conditioning technicians. Instead, these individuals recharge the systems themselves using small cans of HFC-134a purchased in auto-parts stores. This practice has the potential to release significant amounts of HFC-134a to the air. Emissions can result from incorrect recharging techniques and procedures on the part of these non-professionals, and from the discarding of partially full cans following recharging. Even if the individual attempts to transfer all of the can's HFC-134a into the air conditioner, some small amount, referred to as the "heel," will inevitably remain in the can and will be released during can disposal.

The amount of refrigerant emitted to the air from non-professional operations has not been quantified accurately. Upper bounds for this HFC-134a emissions source have been made by Delphi Corporation on the basis of US EPA estimates of total amount of HFC-134a sold for motor vehicle recharging and from industry data for professional air conditioning service. This difference, which is attributed to the non-professional do-it-yourself (DIY) user, amounts to approximately 40 million pounds of HFC-134a per year, nationwide. In order to improve these estimates for California, much better data is needed on: 1) the number of small cans of HFC-134a for retail sale to non-professionals, 2) the amount of HFC-134a in the can "heel", 3) the amount of refrigerant that is discarded. This information would allow for a better evaluation of the potential extent of the small can problem.

**PREVIOUS WORK:** ARB staff is not aware of any experimental data showing how much HFC-134a is emitted from the recharging of motor vehicle air conditioners by non-professionals, or the amount of HFC-134a remaining in small cans after recharging by non-professionals. The estimates of emissions from small cans have been made on the basis of assumed can heels. The US EPA is considering sponsoring a study to estimate the amount of HFC-134a that remains in small cans when they are disposed of by non-professionals following system recharges. ARB staff were invited to be part of a project stakeholder advisory group. Thus, results from EPA's study will complement the proposed California-specific investigation.

**OBJECTIVE:** The objective of this project is to obtain experimental data to support an estimate of the potential impact of emissions of HFC-134a from non-professional servicing of motor vehicle air conditioning systems. Included in this work is the collection of data on the number of small cans sold in the state, the can heel, and the amount of HFC-134a in small cans that is not transferred to a vehicle AC system due to improper recharging techniques.

**DESCRIPTION:** A series of experiments could be designed and conducted in which vehicles with varying levels of air conditioning refrigerant levels were recharged using small cans by non-professional individuals who perform their own system recharging.

Estimates of leakage during recharging could be made by evacuating the systems following recharge in these experiments, and comparing the amount of HFC-134a recovered with the original amount in the small cans. Can heels could be determined by measuring the amount of HFC-134a remaining in the can after recharges that are determined to completely fill the system. The likelihood of using any remaining HFC-134a in the can could be assessed on the basis of the amount remaining. Can heels would be determined on the basis of when the amount of refrigerant remaining in the cans was judged small enough to warrant can disposal. Estimates of the number of cans sold will be made by contacting manufacturers of small cans and suppliers of small cans of HFC-134a.

**BENEFITS:** The results of this study would allow ARB to refine its estimates of emissions of HFC-134a from motor vehicle air conditioning systems by including estimates of emissions that occur from the recharging of systems by non-professionals. A more accurate and refined emissions estimate would allow the ARB staff to better assess the need for and feasibility of further HFC-134a control measures, including regulations directed at non-professional recharging operations.

# TITLE: Impact of Climate Change on the Frequency and Intensity of Low-Level Temperature Inversions in California

**PROBLEM:** Meteorology plays a dominant role in the determination of air pollution concentrations in California. Measurements show that large scale meteorological patterns such as El Niño events can significantly change the frequency and severity of air pollution episodes. El Niño events change meteorological patterns for about one year, and they typically occur every five to seven years. In contrast, climate change refers to a sustained shift in meteorological patterns that occurs over a longer time period. It is expected that climate change will significantly affect meteorological patterns in California over the next decade and longer. The implications of climate change on air quality problems in California are largely undetermined.

Low-level atmospheric temperature inversions (where temperature increases with height) inhibit vertical movement of air and can thereby increase the concentrations of pollutants near the ground. As the climate and regional circulation patterns change, the frequency and intensity of low-level temperature inversions will be impacted in an unknown manner. A variation in the frequency or intensity of these low-level inversions would likely have a significant impact on air quality in California.

**PREVIOUS WORK:** Previous studies have examined the effect of climate on regional air quality in the central and eastern portions of the United States (Hogrefe et al., 2004; Mickley et al., 2004). These studies used output from Global Climate Models (GCMs) to study the frequency of large scale weather patterns that promote the formation of air pollution events. The GCM output can also be dynamically downscaled using regional meteorological models to simulate air pollution formation with regional air quality models. The results of these previous studies predict that the frequency of summer ozone air pollution events will increase in the future due to altered climate and increased background concentrations of ozone.

**OBJECTIVE:** To better understand how the frequency and intensity of low-level temperature inversions might vary or change in California in a changing climate. This knowledge could then be used to produce a more accurate estimate of climate-induced changes in air quality in California during the next few decades.

**DESCRIPTION:** Analysis of low-level inversions during the approximately five decade historical period can be used to project the frequency and intensity of low level inversions from climate simulations and their impact on air quality over the next century as predicted by different models using different greenhouse gas emission scenarios.

**Part I.** The first part of this project would examine historical climate records from the past 50 years to characterize and better understand the variability of low-level inversions in California. The approach is based on statistical analyses and case studies. This would first entail cataloging the occurrence of low-level inversions and then diagnosing the circulation patterns, both large-scale and regional, that cause or are associated with them. Local meteorological variables (such as surface wind speed,

stability, relative humidity, offshore sea surface temperature) and seasonal difference would also be examined. Associated with this effort is the need to recognize low-level inversions from the measures that are available from global circulation models (GCMs). For the historical period, these measures might be extracted from "observed" large scale atmospheric structure via one of the reanalysis model datasets. The results from the first part of the study would be used to recognize the occurrence of low-level inversions, and address whether warmer periods in the observed record are associated with more inversions or more intense inversions. Once this cataloging of the circulation patterns and mixed layer variables is completed, the project would focus on determining how these circulation patterns and mixed layer variables are influenced by inter-annual to decadal climate modes such as the El Niño-Southern Oscillation.

**Part II.** The second part of the project would use the results of Part I to project the frequency and intensity of low-level inversions in future climate scenarios. Here, results from GCM runs would be examined to determine the frequency and intensity of low-level inversions over the next century. Multiple runs from different ensemble members (if available), and different climate GCMs would be used to help assign a statistical significance to the results. Additionally, model runs produced with different greenhouse gas emission scenarios would be used to estimate the possible range of low-level inversion variability. Are GCM results consistent across spring, summer, fall and winter seasons? Is the change in inversion characteristics directly related to the changes in temperature (warming) or are other circulation measures involved as a fundamental determinant?

**BENEFITS:** Some of the key air pollutants (ozone, secondary particulate matter) depend on temperature or upon the vertical gradient of temperature (e.g. inversion strength) in the lower atmosphere. Virtually all climate model projections indicate that California's climate will warm as greenhouse gases continue to accumulate in the atmosphere. Based upon recent runs over a variety of models and greenhouse gas emissions scenarios, potential warming over California during the 21<sup>st</sup> century would range from about 2°C to 5°C (change of temperatures in 2100 relative to recent 1961-1990 historical climatology). Because the magnitude of these changes may rival or exceed the magnitude of natural year-to-year climate variability in California, these changes could have significant consequences on the production and buildup of air pollutants in California's air basins. Thus, a better understanding of future changes in low level inversions and the associated atmospheric structure is crucial to preparing for regional air quality problems in California over the next several decades.

### TITLE: Economic Impacts and Benefits of Climate Change Control Strategies

**PROBLEM:** The strategies to reduce climate change emissions would impact the California economy positively and negatively. Experience indicates that because most climate change strategies strive for efficiency improvements, the economy would benefit because more products and services are produced from less resources for the benefit of the consumer. More efficiency implies increased income which when invested or spent creates jobs. However, some economic sectors such as petroleum would realize negative impacts. Less fuel consumption would lead to lower profits and jobs for the petroleum sector. Experience with economic modeling and analysis shows that the positive impacts on the economy outweigh the negative. To fully understand and estimate the impacts the economic model updates and improvements are needed. This research would address the economic modeling needs.

**PREVIOUS WORK:** ARB has used Environmental Dynamic Revenue Analysis Model (E-DRAM) for several years to evaluate statewide economic impacts of major regulations and plans. E-DRAM, computable general equilibrium (CGE) model, is the work of Professor Peter Berck of the Department of Agricultural and Resource Economics (ARE) at UC Berkeley. He created the model for the California Department of Finance to analyze tax policies. ARB subsequently has funded further development ARB used E-DRAM to assess the economic impact of State of the model Implementation Plans, reformulated gasoline regulations, the petroleum dependency study with the California Energy Commission, the AB 1493 motor vehicle climate change regulations, and the Climate Action Team plan for Cal/EPA. Professor David Roland-Holst, also at ARE, has developed the Berkeley Energy And Resources (BEAR) model, a follow-on to E-DRAM. BEAR follows dynamic response of the economy to shocks, whereas E-DRAM shows only a snapshot of the final post-shock equilibrium. Both E-DRAM and BEAR share a Social Accounting Matrix (SAM) based on industrial data from 2003. REMI is another model, capable of county-level aggregation, used by some states and many local governments but not by the State of California.

**OBJECTIVE:** The objective is to improve ARB's in-house capability to model the economic impact of climate change control strategies.

**DESCRIPTION:** The contractor will develop a CGE model of the California economy with these features:

- Integrate E-DRAM and the BEAR model,
- Improve the resolution of the SAM by
  - Breaking out the Transportation sector into Ports, Ships, Rail, Trucks, Goods Movement between ports and destinations outside of California
  - Breaking out Solar Electricity, Ethanol, Renewable Electricity Generation
- Develop a SAM based on industry data for 2006 or 2007,
- Project a SAM for 2010 and 2020 based on trends likely to influence growth of different sectors,

- Scrutinize and if possible improve the trade elasticities assigned to industrial sectors, and
- Deliver the model and input files in a human-readable and editable form, such as GMS (GAMS files) or XLS (Microsoft Excel files); in other words, not an executable compiled from contractor-held source code.

**BENEFITS:** This project will enhance ARB's in-house ability to model economic impact of major regulations and plans. This benefit is not limited to climate change control strategies. State Implementation Plans and major regulations would benefit as well. ARB is gradually improving the sophistication of its economic analysis. The next logical step is to continue to improve E-DRAM and to capture the new features built into the BEAR model.

#### TITLE: Conduct Tropospheric Ozone Model Simulations to Reproduce Observed Long Term Trends in Background Ozone Levels

**PROBLEM:** Current models have difficulty reproducing the observed trends in background tropospheric ozone over the 20th century and over the past few decades. This inability raises questions as to our understanding of the natural sources of ozone precursors and their possible perturbation by human activity. The precursor gases to tropospheric ozone - nitrogen oxides ( $NO_X$ ), volatile organic compounds (VOCs), and carbon monoxide (CO) number- through related chemistry influence hydroxyl (OH) radical concentrations (key atmospheric oxidants) and hence the lifetime of methane, another major greenhouse gas. In turn, methane is a major precursor for the tropospheric ozone background. Methane has shown variable trends over the past decades that are poorly understood and could provide important information on its sources.

**PREVIOUS WORK:** A number of studies have used global chemical transport models and future emission scenarios to predict future ozone concentrations. Zeng and Pyle (2003) predict climate change increases tropospheric ozone due to enhanced stratosphere-troposphere exchange. The effect of changes in both climate and emissions has also been considered in a number of model simulations [e.g., Brasseur et al., 1998; Grewe et al., 1999, 2001; Johnson et al., 1999, 2001; Stevenson et al., 2000; Grenfell et al., 2003]. A directed study of the eastern U.S. (Hogrefe et al., 2004) found that, around 2050, climate change would be the most important factor leading to increases in the upper quartile of 8-hour average surface ozone concentrations, whereas projected changes in anthropogenic emissions would cause increases only half as large. Tropospheric ozone is formed by photochemical reactions involving emissions of methane and pollutants and is the third most important greenhouse gas after carbon dioxide and methane. One of the poorly understood feedbacks of potential importance is atmospheric chemistry feedback, due to chemical interactions affecting ozone concentrations.

There are two direct ties between background ozone and California issues. It will be almost impossible to achieve the ozone targets in California if background ozone concentrations continue to rise. Recent ARB funded studies also suggest that background ozone may promote the formation of PM nitrate during winter stagnation episodes. Background ozone strongly contributes to the nighttime formation of particulate nitrate through the formation of N<sub>2</sub>O<sub>5</sub> in the upper atmosphere during the evening hours. This increased nitrate production compensates for the partitioning of nitric acid back to the vapor phase as temperatures are raised. California currently has the highest PM concentrations in the country, with PM nitrate forming a major component during the most severe episodes. Any change in background ozone that encourages nitrate formation is a direct California issue.

**OBJECTIVE:** The objectives of are to better understand the factors controlling the concentrations and trends of tropospheric ozone, and its impact on future air pollution events in California.

**DESCRIPTION:** Trends in tropospheric ozone (the third-most influential anthropogenic greenhouse gas) are not well determined and are driven by a mix of emissions, including regional pollutants and  $CH_{4}$ . Satellite data recently obtained and to become available for the first time for methane, tropospheric ozone, and tropospheric aerosols will be analyzed and interpreted in the context of global models and assimilation systems. The results will also form part of a detailed global survey of past and future trends for tropospheric ozone and its precursor species. The focus of this work will be on areas most likely to impact California's air quality.

Existing climate model results will be evaluated by exploiting new/improved observational data such as satellite and aircraft, as well as surface observations of tropospheric composition and underlying processes. Using regional air quality models, a detailed perturbation analysis will be carried out to study the effect of meteorology and background concentrations on ozone and PM2.5 concentrations during present-day and future air pollution events. A limited number of global climate model (GCM) runs may be performed to provide the inputs necessary for the California regional air quality modeling.

**BENEFITS** There are two direct ties between background ozone and California issues. It will be almost impossible to achieve the ozone targets in California if background ozone concentrations continue to rise. Background ozone concentrations are also predicted to increase in the future, leading to increased PM2.5 concentrations in California's air basins. This project will provide major advances on this problem by exploiting observational data of tropospheric composition and underlying processes to improve global ozone models. This project will also improve the ability of global modeling to reproduce observed long-term trends in background tropospheric ozone, and its impact on future air pollution events in California.

**COST:** \$300,000